

STUDIES IN THE FLUORANTHENE SERIES

by

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Thesis for Degree of Doctor of Philosophy.

May 1948.

University of Edinburgh.

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INTRODUCTION.

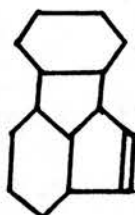
The first reported isolation of the hydrocarbon now known as fluoranthene was made in 1844, when Boedeker (Ann., 1844, 52, 100) described the isolation of 'Idryl', from 'stupp', a mixture of hydrocarbons obtained by distilling mercury ores at Idria. He quoted its m.p. as being above 100°C. and gave it the formula $C_{42}H_{14}$, which is equivalent in modern theories to $C_{15}H_{10}$.

Goldschmidt (Ber., 1877, 10, 2024) followed up Boedeker's work and isolated idryl from the same source quoting its m.p. as 110°C. In the same year Fittig and Gebhard reported the separation, from the higher boiling fractions of coal tar, of a hydrocarbon which they called fluoranthene and identified it with Goldschmidt's idryl.

Since then other sources of fluoranthene have been discovered. Mayer and Tager (Ber., 1920, 53B, 1264) found it in the higher boiling fractions of acetylene tar, produced by leading acetylene, mixed with hydrogen, through a porcelain tube at 640-650°C. It also occurs with other polycyclic aromatic hydrocarbons in the products of the reductive fission of bituminous and lignin containing substances. Recently John Rehner Jr. (J.A.C.S., 1940, 62, 2243) has separated/

separated fluoranthene from carbon black.

In 1878 Goldschmidt (Ber., 1878, 11, 1578) described its isolation from mercury ores using xylene, and its purification, while Fittig and Gebhard (Ann., 1878, 193, 142) supported Boedeker's and Goldschmidt's analytical figures and ascribed to fluoranthene the formula $C_{16}H_{10}$. In the same paper Fittig and Gebhard described the preparation of a picrate, dibromo- and trinitro-derivatives, and of fluoranthene quinone. They also obtained from the oxidation of fluoranthene, fluorenone-1-carboxylic acid, and on treating this with potassium hydroxide obtained diphenyl-2:3-dicarboxylic acid. From these experiments they suggested the following formula for fluoranthene:

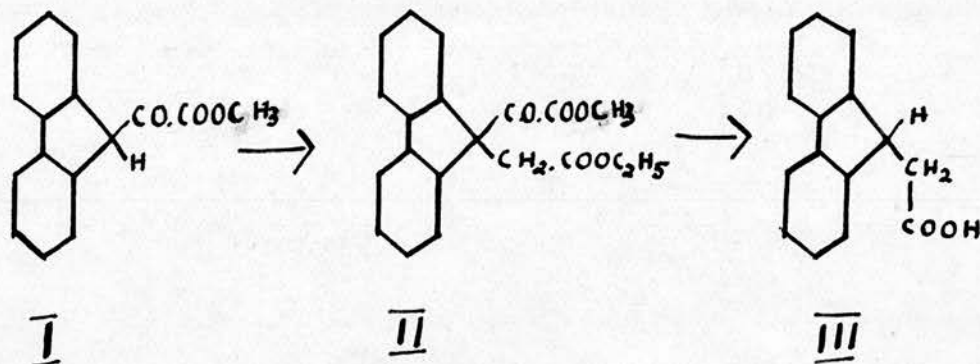


Fittig with another co-worker, Liepmann (Ann., 1880, 200, 1) followed up his previous work by describing its separation from coal tar, and giving further details in his study of its oxidation products. They reported/

reported the formation of a complex between fluoranthenequinone and the hydrocarbon, and described the reduction of fluorenone-1-carboxylic acid to the corresponding fluorene carboxylic acid, which on distillation with lime yielded fluorene. Goldschmidt (Wien. Abad. Ber., 1881, 81, 415) reported the reduction with phosphorus and hydriodic acid to $C_{15}H_{12}$ and at higher temperatures to $C_{15}H_{18}$, and supported the work of Fittig and Gebhard by ascribing the same structural formula to fluoranthene. He also described the preparation of tribromo- and trichlorofluoranthene, the preparation of the sulphonic acid, and its conversion, via the cyanide to the carboxylic acid. Later Goldschmidt (Monats., 1902, 23, 886) continued his work on the oxidation of fluoranthene with a description of the various derivatives of fluorenone-1-carboxylic acid. He described the preparation of 1-aminofluorenone from the acid amide, and that of the 1-hydroxyfluorenone by the diazotisation of the aminofluorenone.

A lull in the chemistry of fluoranthene followed until Fritz Mayer (Ber., 1913, 46, 2579) very nearly succeeded in synthesising fluoranthene. He effected the synthesis of 9-fluorenyl acetic acid from methyl-1-keto-1-(9-fluorenyl)-acetate (I) by the elimination of hydrogen bromide between this compound and ethyl bromacetate/

bromacetate and hydrolysing the resulting compound(II) with aqueous caustic soda, the 1-keto acetic ester group being destroyed to leave the fluorenylacetic acid (III).

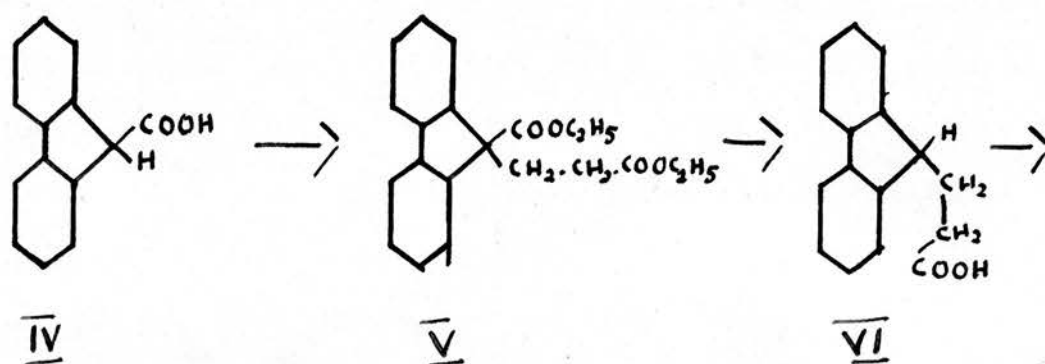


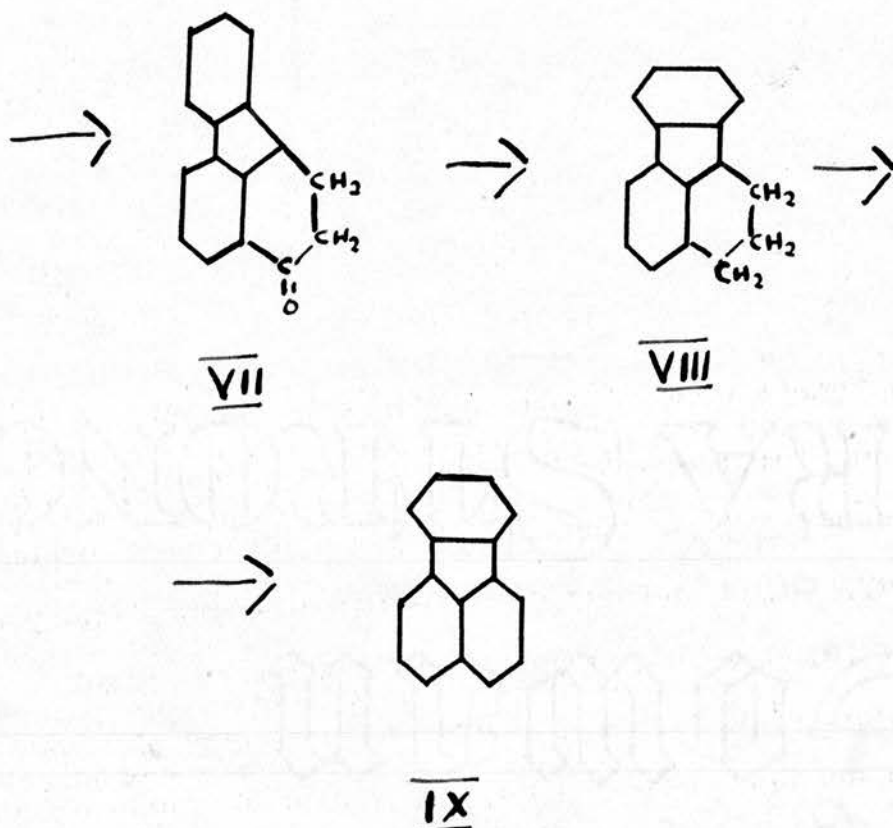
He did not, however, succeed in cyclising this acid: had he done so he would have synthesised a derivative of fluoranthene corresponding to the structural formula of Goldschmidt and Fittig.

Meyer also prepared the 9-fluorenyl-2-propionic acid by the same method using ethyl 2-iodopropionate instead of the ethyl bromacetate, but again could not effect the ring closure.

The chemistry of fluoranthene again remained untouched for some years until Von Braun and Anton (Ber., 1929, 62, 148) pointed out that the conception of fluoranthene as a derivative of indene was not in keeping with their work on the stability of ring systems. The presence of one more carbon atom in the molecule would not greatly influence the analysis figures/

figures, they argued, while the observed facts could be readily explained if fluoranthene were a derivative of naphthalene, rather than of indene. They followed up their suggestion by a synthesis of fluoranthene, which established its constitution as a derivative of naphthalene. Their experimental work was in part a repetition of that of Fritz Mayer in that they used his synthesis of 9-fluorenylacetic acid, but also could not effect the ring closure. Their synthesis of the 9-fluorenyl-2-propionic acid was slightly different. They started from the 9-fluorenyl carboxylic acid (IV) and by treating it with ethyl-2-iodo-propionate in alcoholic caustic soda, they finally obtained ethyl-9(9'-carbethoxyfluorenyl)-2-propionate (V) which on hydrolysis and decarboxylation yielded 9-fluorenyl-2-propionic acid (VI). The fluorenyl propionic acid was converted to the acid chloride by means of thionyl chloride, and the ring closure effected by means of aluminium chloride in light petroleum. The cyclisation product 4-keto-1:2:3:4-tetrahydrofluoranthene (VII) was reduced by the Clemmenson method to give 1:2:3:4-tetrahydrofluoranthene (VIII) which was dehydrogenated by lead oxide to fluoranthene (IX).

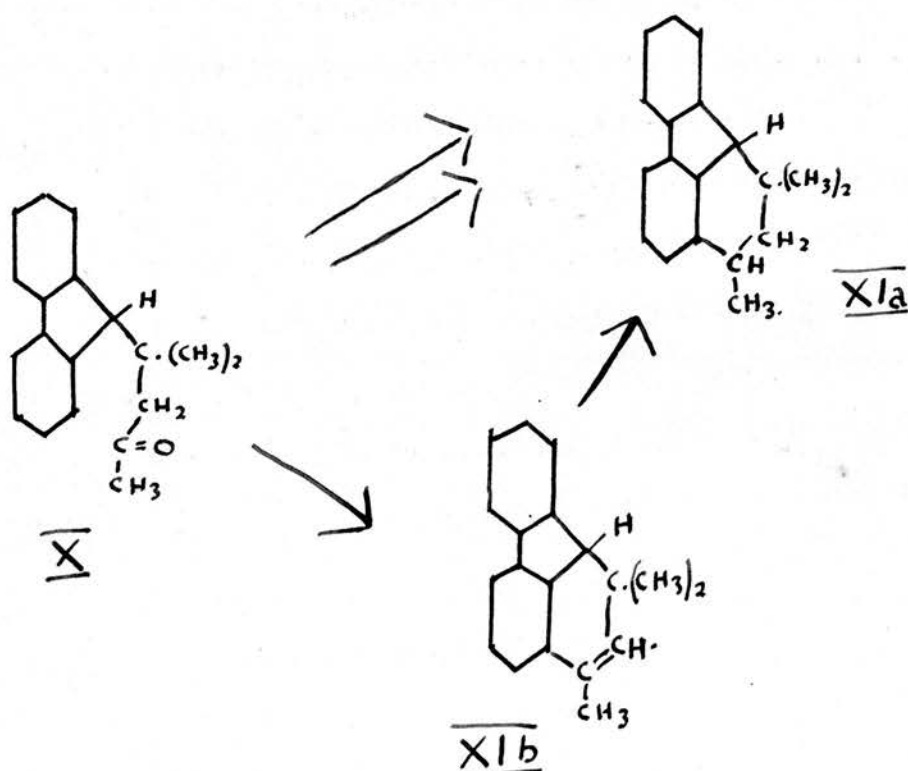


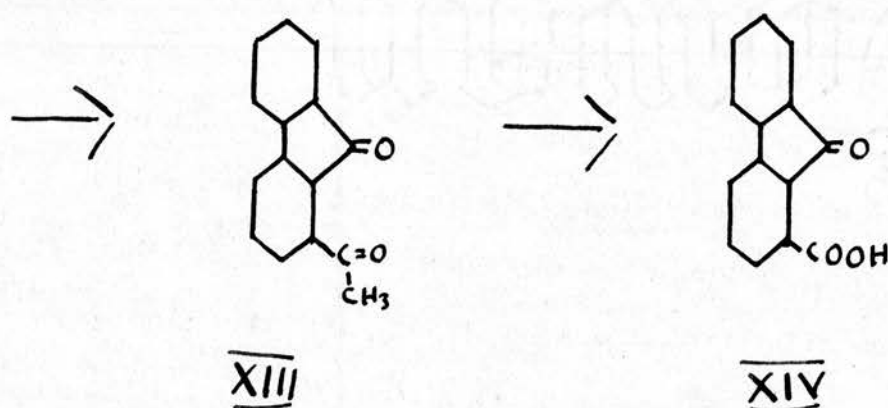
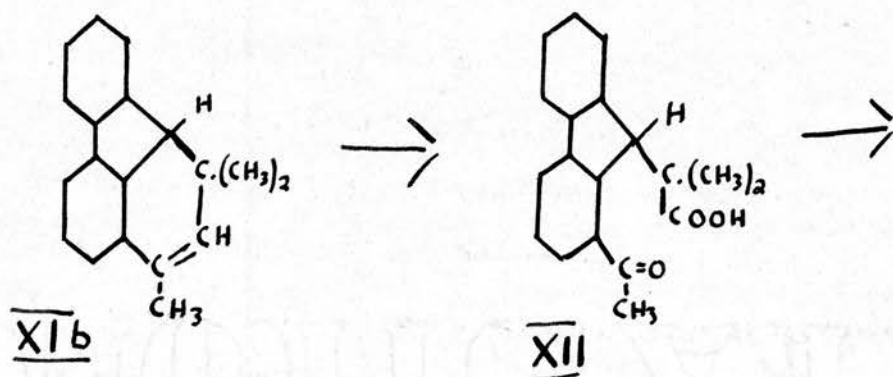


Another synthesis of fluoranthene has since been effected by Cook and Lawrence (J.C.S., 1936, 1431) starting from 1-(1'-naphthyl)-2-methyl- Δ^1 cyclohexanone, and more recently by Orchin and Reggel (J.A.C.S., 1947, 69, 505) have also effected a synthesis in three stages from naphthalene. They prepared 1-phenylnaphthalene, from naphthyl magnesium bromide and cyclohexanone, and dehydrogenating the product of this reaction. Cyclodehydrogenation of the 1-phenylnaphthalene gave fluoranthene.

France/

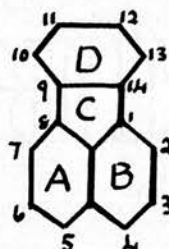
France, Maitland and Tucker (J.C.S. 1937, 1739) in their experiments on the condensation of fluorene with acetone, obtained methyl-9-fluorenyl-2-methyl-n-propyl-ketone (X) and obtained from this an undetermined compound which later France, Tucker and Forrest (J.C.S., 1945, 7) proved to be 2:2:4-trimethyl-1:2-dihydrofluoranthene (XIa). In this paper they also gave a method for its hydrogenation to 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene (XIb), a compound for which they give two other methods of preparation by cyclisations of their original ketone. They proved the structure of these compounds by a three stage oxidative degradation of their original fluoranthene derivative into 1-acetylfluorene-9-isobutyric acid (XII), 1-acetylfluorenone (XIII) and fluorenone-1-carboxylic acid (XIV).





It/

It is appropriate at this point to give the numbering of the fluoranthene molecule, which is now in general use which will be used throughout this thesis.

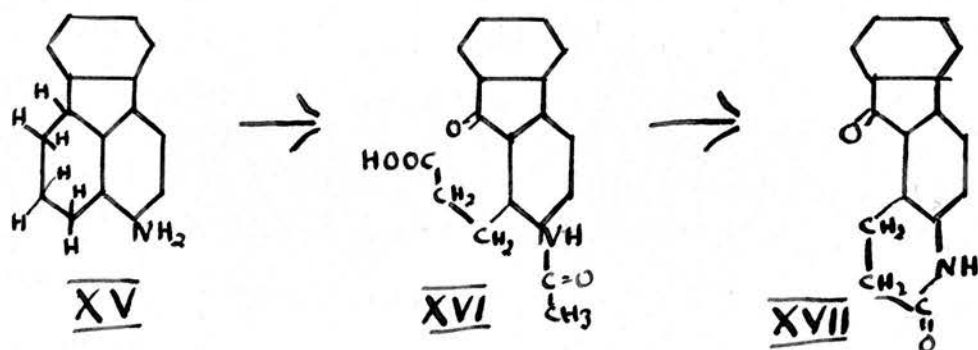


Von Braun and Manz (Ber., 1930, 63, 2608) studied the hydrogenation of fluoranthene and found it occurred successively in rings B and D, 1:2:3:4-tetrahydrofluoranthene being formed with sodium amalgam and alcohol, whereas hydrogenation with nickel in decahydronaphthalene gave 1:2:3:4:9:10:11:12:13:14-decahydrofluoranthene.

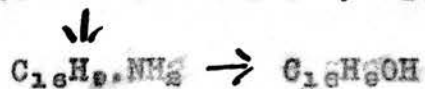
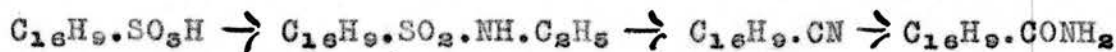
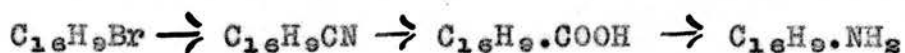
The following year, von Braun and Manz published the important results of their work on monosubstitution (Ann., 1931, 488, 111). Not only did they prepare bromo-, nitro-, amino-, hydroxy-, and sulphonic acid derivatives, but they succeeded in determining the positions occupied by these substituents.

There/

There are five possibilities for mono-substitution (i.e. 2, 3, 4, 12 or 13). Von Braun suspected that substitution occurred mainly in position 4, and was able to prove this supposition in the following way. Amino-fluoranthene was reduced to the 5:6:7:8-tetrahydrofluoranthene (XV), the acetyl derivative of which was oxidised to the keto carboxylic acid (XVI). The deacetylated acid passed readily to the lactam (XVII) with the loss of water, showing that the original compound must be 4-aminofluoranthene.

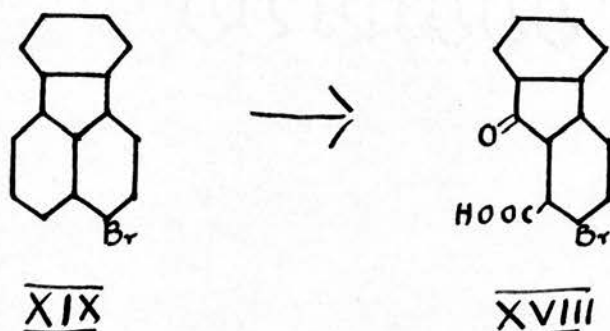


The main derivatives, bromo-, nitro-, and sulphonic acid are readily converted to the same aminofluoranthene, or to the cyanide obtained from it as outlined below.



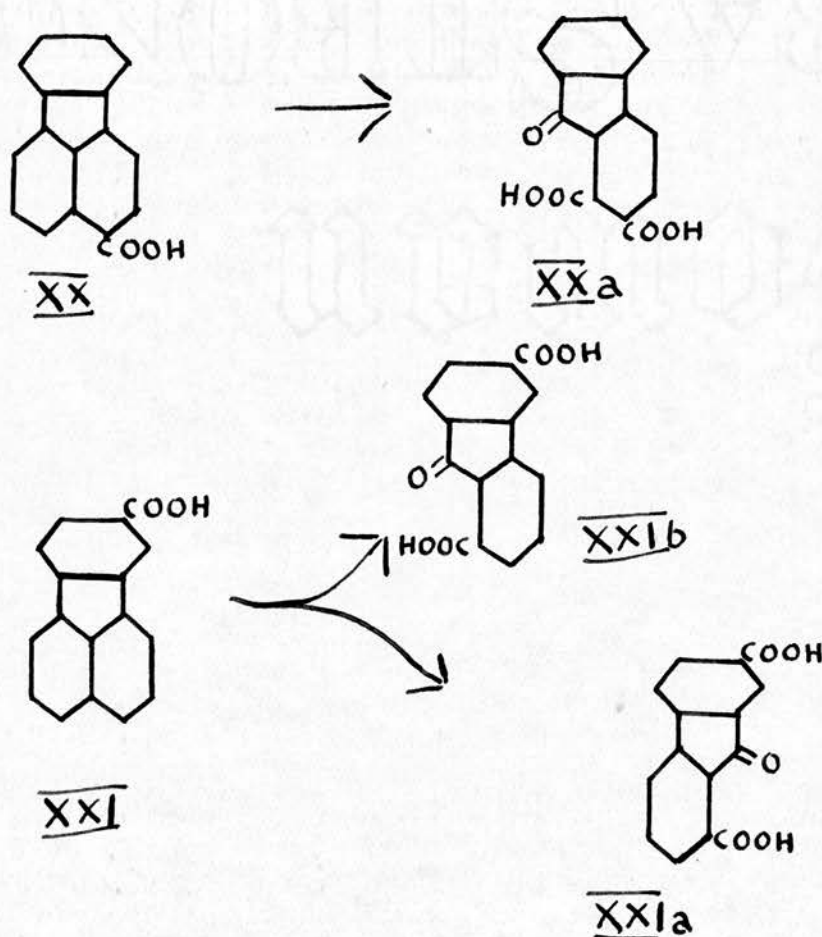
Von Braun therefore concluded that monosubstitution occurs mainly in the 4-position. He also showed that monosubstitution also occurs in the 12-position though to a very small extent.

These authors continued their work (Ann., 1932, 496, 170) by oxidising monosubstituted nitro- and bromofluoranthenes to fluorenone-1-carboxylic acids and supposed that 2:bromofluorenone-1-carboxylic acid (XVIII) had been obtained from the 4-bromofluoranthene (XIX).



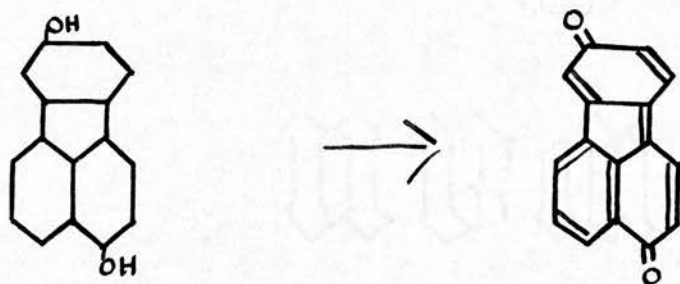
In contrast to the orientation of the previous derivatives, von Braun in the above paper showed that acylation of fluoranthene proceeded mainly in the 12-position, together with small amounts of the 4- and diacyl derivatives. Acylation in the 12-position was shown by the conversion of benzoylfluoranthene to the 12-amino compound. The fact that we get both 4- and 12-derivatives was proved by the oxidation of the two/

two fluoranthene carboxylic acids to the corresponding fluorenone dicarboxylic acids. The 4- (XX) yield one acid, fluorenone-1:2-dicarboxylic acid (XXa), whereas the 12- form (XXI) yielded a mixture of acids separated as the esters of fluorenone-1:7-dicarboxylic acid (XXIa) and fluorenone 1:6-dicarboxylic acid (XXIb).

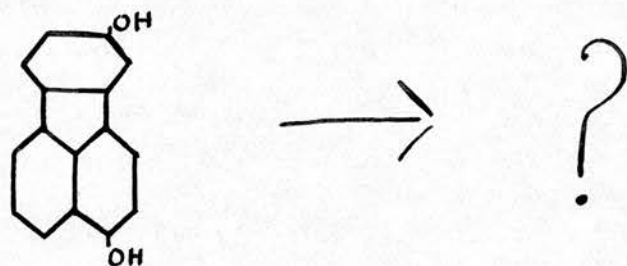


Tobler, Holbro, Sutter and Kern (Helv. 1941, 24, 100E) showed how 4-bromofluoranthene could be obtained from the readily available 4-bromo-5:6:7:8-tetrahydrofluoranthene, gave a description of an improved method of/

of obtaining dibromo-5:6:7:8-tetrahydrofluoranthene. They also prepared a dihydroxy derivative which was readily oxidisable to a quinone. From their obtaining this compound they postulated that disubstitution in the fluoranthene molecule takes place in the 4- and 11-positions as the quinone compound is more readily comprehended and explained by a 4:11 than by a 4:12 substitution as may be seen from the diagrams.



4:11-dihydroxyfluoranthene



4:12-dihydroxyfluoranthene

The attempt to prove this 4:11 disubstitution by synthesis from ethyl-1-keto-1'-(2:7-dibromo-9-fluorenyl) acetate was unsuccessful.

However/

However they were able to synthesise a benzo-homologue of 4:11-dibromofluoranthene by condensing 2:7-dibromofluorene with o-acetaminobenzaldehyde, hydrolysing off the acetyl group, diazotising the amino group with amyl nitrite in benzene containing a little sulphuric acid and cyclising the product by heating the resulting solution. The product obtained was 4:11-dibromo-5:6-benzofluoranthene.

Tobler and Kern are also names which appear quite often in the patent literature in connection with fluoranthene. Quite a large number of patents have been taken out to cover the preparation of both simple substituent and rather more complex derivatives of fluoranthene.

Orchin and Woolfolk (J.A.C.S., 1946, 68, 1727) reported fluoranthene as forming a complex with 2:4:7-trinitrofluorenone. Moureu, Chevin and Rivoal (Bull. Soc. Chim., 1946, 106, 9) reported the synthesis of 9-amido-13-cyano-11:12-benzofluoranthene and in a more recent paper (Compt. Rend., 1946, 223, 951) gave the preparation of the unsubstituted 11:12-benzofluoranthene.

Hoffmann and Tagmann (Helv. Chim. Acta, 1947, 30, 288) following von Braun's reduction of fluoranthene to tetrahydrofluoranthene, and Tucker's synthesis of/

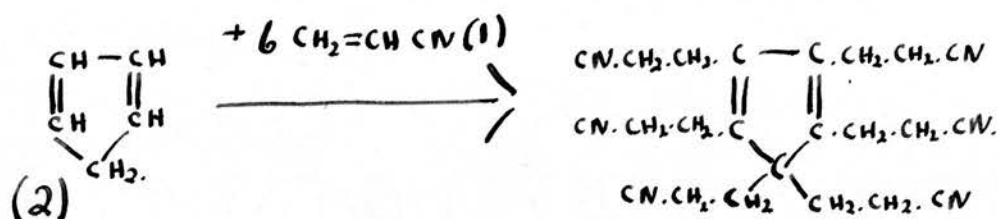
of 2:2:4-trimethyl-1:2:3:4 tetrahydrofluoranthene have formed a series of derivatives of these two compounds, for pharmacological tests, by substituting in the 1-position a series of groups of the 2-chloro-ethyldimethylamine type.

Summarising it may be said that, while our knowledge of monosubstitution of fluoranthene is reasonably extensive and accurate, little is known about disubstitution, though the paper of Tobler, Holbro, Sutter and Kern quoted above gives a line for investigation in this field. The synthesis of substituent derivatives of fluoranthene, the necessary final proof in their orientation has not yet been achieved, and before it can be, much improved and milder methods of synthesising fluoranthene will have to be found.

A brief account of the history of two reactions used in the following work calls for mention.

In 1942 Bruson (J.A.C.S., 1942, 64, 2451, 2851) gave an account of various condensations involving the very reactive double bond of acrylonitrile and the labile hydrogen atoms of various organic compounds in the presence of powerfully alkaline condensing agents. Though caustic soda (40%) or methanolic/

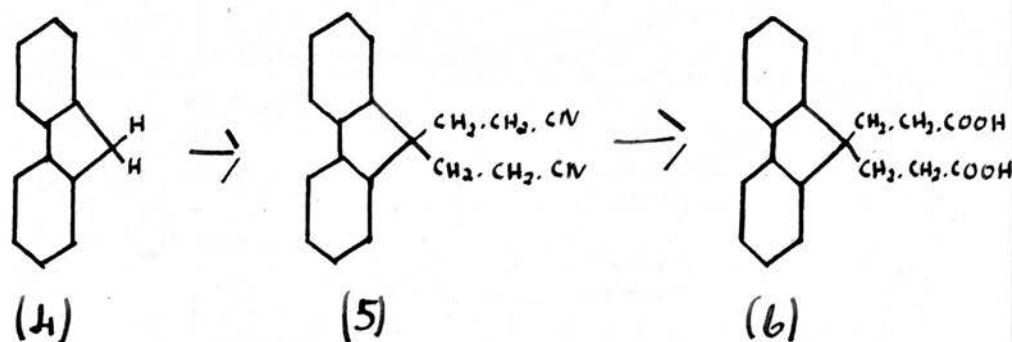
methanolic caustic potash were sometimes effective the best condensing agent was trimethylbenzyl-ammonium hydroxide, marketed in America as a 40% solution under the trade name of 'Triton B', and used catalytically. Perhaps the most striking example of this condensation was that obtained with acrylonitrile (1) and cyclopentadiene (2) when hexa-(2-cyanoethyl) cyclopentadiene is formed.



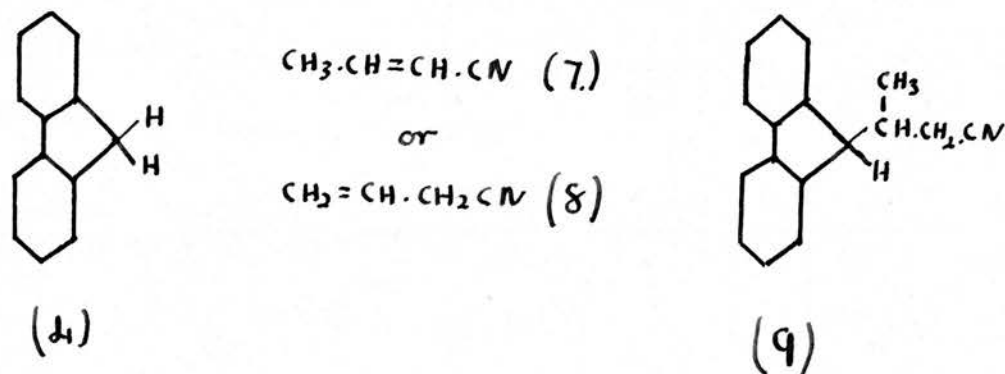
The necessity of a reactive (or labile) hydrogen atom in this reaction was demonstrated in the second paper in which Bruson studied the reaction of acrylonitrile on ketones. With acetophenone he obtained condensation of acrylonitrile with each of hydrogen atoms of the methyl group. However with propiophenone, the condensation only took place on the two hydrogen atoms of the methylene group adjacent to the carbonyl group.

Among the compounds quoted in the first paper as condensing with acrylonitrile was fluorene (4) which has two reactive hydrogen atoms in the 9-position, the/

the resulting compound being bis-9:9'-(2-cyanoethyl) fluorene (5). The cyano groups were hydrolysable to carboxyl groups to give bis-9:9'-(2-carboxyethyl)-fluorene (6).



Bruson also quoted experiments in which he obtained a mono-condensation of croton nitrile (7) or allyl cyanide (8) with fluorene to give the same compound which was 9-(2-cyanoisopropyl)-fluorene (9).

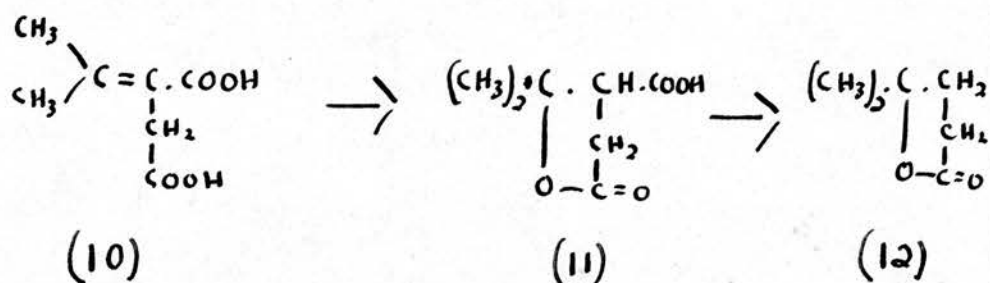


Bruson and his co-workers have since produced in all seven papers on the chemistry of acrylonitrile, the latest being on the subject of 'Cyanoethylation of Ketones and Sulphones' (J.A.C.S., 1948, 70, 214).

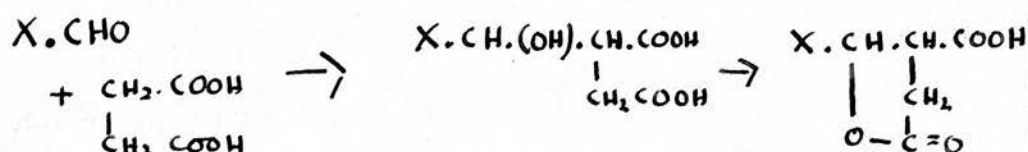
The preparation of such substituted fluorenyl propionic acids, mentioned above, should be useful in the synthesis of fluoranthene derivatives, fluoranthene itself having been synthesised from 9-fluorenyl-2-propionic acid.

The second reaction known as the Stobbe reaction is an alkoxide catalysed reaction between diethyl succinate and a ketone, which Hans Stobbe (Ber., 1893, 26, 2313) discovered as following an aldol rather than the aceto-acetic ester type of condensation which he expected from the work of Claisen and Wislicenus.

Stobbe on treating acetone with diethyl succinate in presence of sodium ethoxide obtained tereaconic acid (10). Treatment with sulphuric acid (50%) gave by lactone formation terebinic acid (11) which with more concentrated sulphuric acid (70%) underwent decarboxylation to 3:3'-dimethylbutyro- γ -lactone (12).



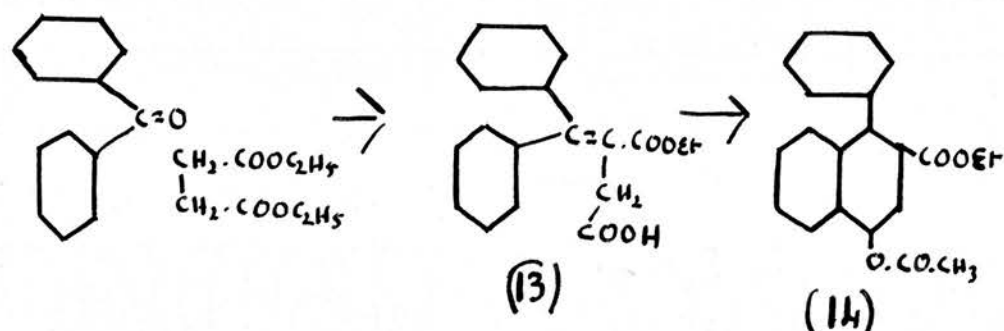
Stobbe also pointed out the similarity of this condensation to the condensation and lactonisation obtained by Fittig (Ann., 1889, 255, 1) between aromatic aldehydes and succinic acid in presence of acetic anhydride.



Stobbe followed up this paper in the following year (Ann., 1894, 282, 281) by giving a general method for these reactions. He showed the condensation resulted in the formation of a half-ester with benzophenone, acetophenone or methyl ethyl ketone, in the latter two cases, isomeric acids being obtained from the half esters produced. He gave a more detailed study of the benzophenone condensation¹ in another paper (Ann., 1894, 308, 89) and later reported the condensation of diethylmethylsuccinate with fluorenone to give 1-methyl-3:3'-diphenylene-2-carboxyvinylacetic acid, though this was obtained in small yields with another unidentified substance (Ber., 1904, 39, 1068).

W. Borsche (Ann., ~~1906~~, 524, 9) was the first to prove the synthetic possibilities of this reaction when/

when he repeated Stobbe's condensation on benzophenone, and cyclised the product 3:3'-diphenyl-2-carbethoxyvinylacetic acid (13) by acetic anhydride and sodium acetate to 1-phenyl-2-carbethoxy-4-acetoxynaphthalene (14).



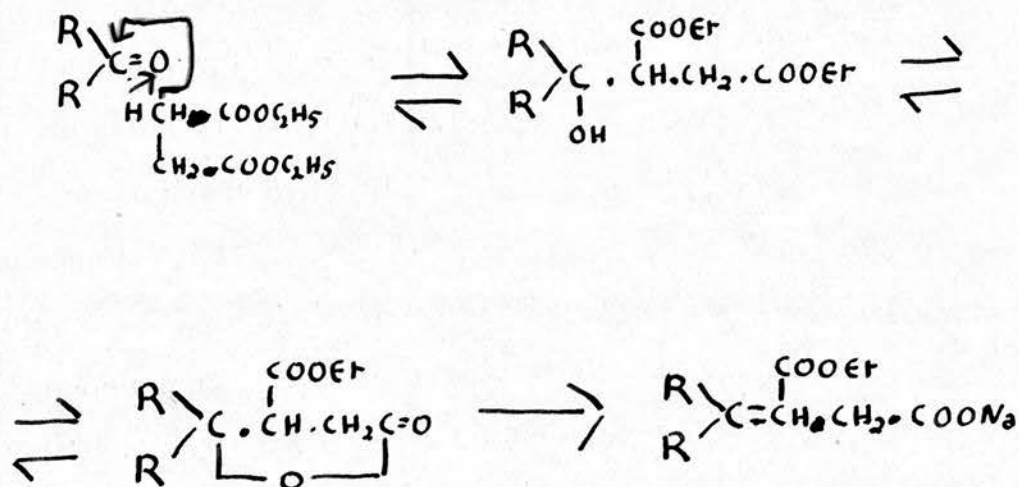
C.L.Hewitt (J.C.S., 1942, 585) was next in the field when he carried out the diethyl succinate condensation with deoxybenzoin, 2-benzoylnaphthalene, and 6-benzoyltetralin, separated the isomeric acids, and cyclised the resulting isomeric acids from deoxybenzoin. Cook and Preston (J.C.S., 1944, 553) repeated Hewitt's condensation with 2-benzoylnaphthalene and from a 2-stage cyclisation on one of the isomers obtained 1:2:5:6-dibenzofluorene.

However it was left to W.S.Johnson and co-workers in America to make a detailed study of the Stobbe/

Stobbe reaction, to improve the old method and to standardise a new technique for the introduction of propionic acid side chains at the site of a carbonyl group by this means.

The original Stobbe method was rather a lengthy process often involving several days but Johnson and his co-workers modified the procedure to give much purer and better yields of the product in a much shorter time. Instead of sodium ethoxide they found potassium t-butoxide to be a more effective condensing agent. With α -tetralone, for example, the original Stobbe condensation produced at the best an 82% yield of a dark semi-crystalline mass after five days, but Johnson (J.A.C.S., 1945, 67, 1360) with potassium t-butoxide obtained yields as high as 96% of a colourless crystalline half ester after a reaction period of forty minutes. Similar results were obtained with other ketones.

The ideas expressed in their paper on the mechanism of this reaction followed from Stobbe's analogy of this reaction to Fittig's experiments (loc. cit.).



In their first papers on the subject Johnson and Goldman (J.A.C.S., 1944, 66, 1030; 1945, 67, 430) applied the original Stobbe method and a modification using sodium ethoxide in ethanol to effect the condensation between 2-acetylnaphthalene and diethyl succinate. They cyclised the resulting isomeric half-esters to

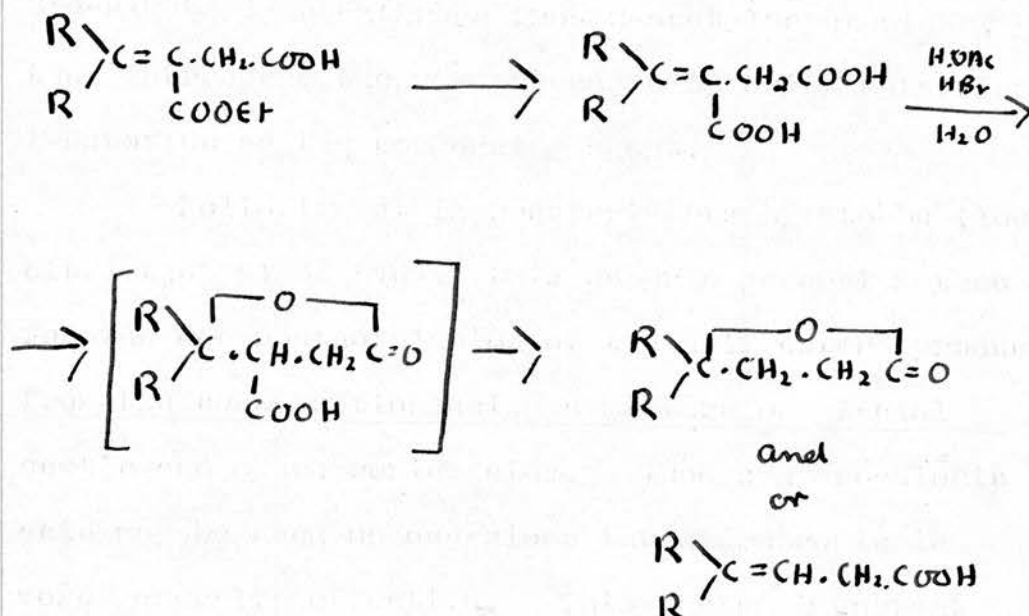
- (1) ethyl 4-acetoxy-1-methyl-phenanthrene-2-carboxylate
- (2) ethyl 3-methyl-6:7-benz-1-indene-2-acetate.

However in the next paper in which Johnson, Goldman and Schneider (J.A.C.S., 1945, 67, 1357) synthesised 2:4/

2:4-dimethylphenanthrene from 2-acetylnaphthalene, they introduced the new procedure by using potassium t-butoxide as the condensing agent.

Following similar experiments by Stobbe (loc. cit.) they also gave in this paper a general method for the decarbethoxylation of the half ester products from the condensation using a mixture of glacial acetic and hydrobromic acids. Though hydrochloric acid may be used on occasions the hydrobromic is more generally effective. This was an important part of the Americans' work as it left a three carbon atom side chain, which is most useful in synthetic cyclisation work, and it also destroyed the isomerism displayed by the half ester condensation products from mixed ketones.

The product from the decarboxylation was either a γ -lactone or the unsaturated acid. In a later paper Johnson, Peterson and Schneider (J.A.C.S., 1947, 69, 74) investigated the condensation products from benzophenone, acetophenone, and tetralone-1, studied their decarbethoxylation and lacto-enoic tautomerism. They submitted evidence to show that decarboxylation invariably goes through the lactone.



The lactone or the unsaturated acid or the mixture thereof could then be reduced to the appropriate propionic or butyric acid.

Other papers on this reaction included cyclisation of the condensation product with tetralone-1 after decarboxylation to 3:4-dihydro-1:2-cyclopentanononaphthalene (Johnson, Johnson and Peterson, J.A.C.S., 1945, 67, 1360), and the synthesis by Johnson and Peterson (Ibid. 1366) of 3'-keto-3:4-dihydro-12-cyclopentanophenanthrene from 1-keto-1:2:3:4-tetrahydrophenanthrene.

The most recent paper in this series was a new/

new synthesis of cadalene by Johnson and A. Russel Jones (J.A.C.S., 1947, 69, 792) in which the initial reaction was a modified Stobbe condensation of diethyl succinate with methyl-p-tolyl ketone.

After such work the synthesis of 9-fluorenyl-2-propionic acid, a stage towards the synthesis of fluoranthene, from fluorenone and diethyl succinate, seems feasible.

Object of Research.

As fluoranthene had been synthesised from 9-fluorenyl-2-propionic acid, the initial object of research was to improve this method and to synthesise derivatives of fluoranthene, by the introduction of a propionic side chain into the 9-position of the fluorene molecule by the following two methods:

(1) The trimethylbenzylammonium hydroxide catalysed condensation of acrylonitrile with (a) fluorene, to give two propionitrile groups in the 9-position and (b) 9-fluorenyl derivatives, to give one propionitrile group in the 9-position.

Also by a similar condensation of substituted acrylonitriles (e.g. phenylacrylonitrile, i.e. cinnamitrile) with fluorene to give 9-fluorenyl-2-propionitriles with a substituent in the side chain.

(2) The Stobbe condensation of 9-fluorenone and diethyl succinate. This, however, proved to be a rather capricious reaction, entailing a detailed study of its products, before further progress could be made. A considerable part of the research therefore had to be devoted to this side issue.

EXPERIMENTAL SECTION

Introduction

This section contains the details of the experimental results obtained throughout the course of this research. The percentage yields quoted are of the maximum theoretical amounts obtainable. Melting points were determined on the apparatus described in 'Qualitative Organic Chemistry' by Dr. Neil Campbell (p. 7, Fig. 4) and were tested for sharpness on a micromelting-point apparatus similar to that described by Kofler (Mikrochem., 1934, 15, 242).

All analyses were done by Drs. Weiler and Strauss of Oxford.

Preparation of the catalyst for acrylonitrile condensations.

The catalyst used is trimethylbenzylammonium hydroxide in the form of an alcoholic solution.

(1) Preparation of trimethylbenzylammonium chloride.

Trimethylamine (20 g., 0.35 mol.) was passed into benzyl chloride (20 g., 0.16 mol.) contained in a test-tube in a freezing mixture. Excess trimethylamine was necessary as it is very volatile and much escaped into the atmosphere. The benzyl chloride became almost solid, the semi-solid being then transferred to a Buchner funnel, and the unchanged benzyl chloride removed by suction. The white solid remaining was washed several times with small quantities of methanol to remove adhering benzyl chloride.

Yield = 19 g. (64%)

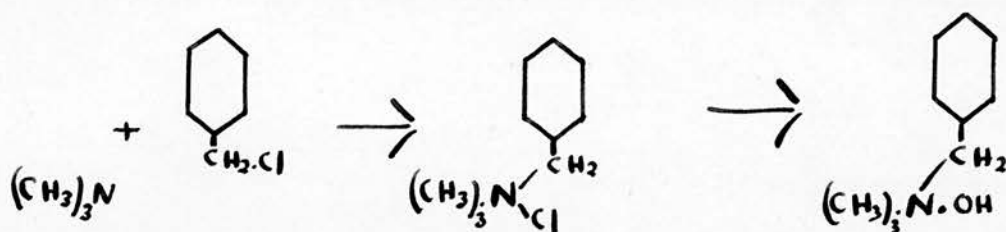
(2) Preparation of trimethylbenzylammonium hydroxide solution.

The method follows that of Walker and Johnson (J.C.S., 87, 955) for the preparation of tetramethylammonium hydroxide. Trimethylbenzylammonium hydroxide (18.5 g.), 0.1 mol.) was dissolved in methanol (30 ml.) and to this was added a methanolic solution of potassium hydroxide (35 ml. containing 6 g. KOH, 0.106 mol.). The mixed solutions were allowed to stand several hours to allow the precipitated potassium chloride to separate/

separate out as completely as possible. .

Weight of KCl = 6.9 g.

This gives a solution of trimethylbenzylammonium hydroxide of approximately 20%.

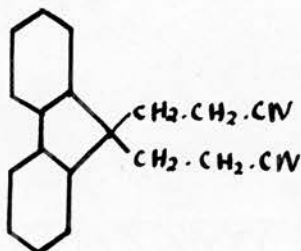


Preparation of bis-9:9' (2-cyanoethyl)-fluorene.

or fluorenyl-bis-9:9'-propionitrile.

cf. Bruson and co-workers,
(J.A.C.S., 1942, 64, 2457)

Acrylonitrile (28 g.)
was added dropwise during 20
mins. to a rapidly stirred
solution of fluorene (41.5 g.)



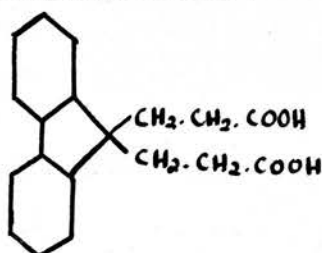
and catalyst (4 ml., 20% solution) in dioxan (125 ml.).
The temperature of the reaction mixture was maintained
between 30-40°C. After all the acrylonitrile had
been added the solution was stirred for another one
and a half hours at room temperature to complete the
condensation and was then added dropwise to water
(200 ml.) to precipitate the compound. This was
filtered, dried at the pump and obtained as a pale
yellow compound, which gave colourless prisms on
recrystallisation/

recrystallisation from ethanol.

Yield = 45 g. (66%)

M.p. = 118-120°C. (Lit. 121°C.)

Hydrolysis of bis-9:9'-(2-cyanoethyl)-fluorene.
to bis-9:9'-(2-carboxyethyl)-fluorene.



Bis-9:9'-(2-cyanoethyl)-fluorene (45 g.) was heated under reflux with a sodium hydroxide solution (16 g. NaOH in 200 ml. water) for 12 hours. Ammonia was given off and the solid gradually dissolved. The final clear solution was bleached with charcoal, cooled and filtered. By addition of concentrated hydrochloric acid to the solution a white solid was obtained, which was recrystallised from ethanol.

Yield = 38 g. (85%)

M.p. = 270-273°C. (Lit. 273-274°C.)

Diethyl ester was prepared, m.p. 107-108°C.

i.e. bis-9:9'-(2-carbethoxyethyl) fluorene.

Analysis: Found: C, 75.93%; H, 6.92%.

$C_{23}H_{26}O_4$ requires C, 75.4%; H, 7.1%.

Attempted/

Attempted Cyclisations on the Above Acid.

(1) Acid chloride - Friedel-Craft method. The acid was converted to the acid chloride by refluxing with excess thionyl chloride and the excess thionyl chloride removed under vacuum. The acid chloride was then refluxed with a monomolecular amount of anhydrous aluminium chloride in light petroleum (b.p. 100-120°). The resulting solution was extracted alternately with ether and sodium hydroxide and the washed and dried ether layer yielded only a small quantity of brown oil but the acidified alkaline solution yielded a white solid. Crystallisation of this from ethanol yielded a white solid, m.p. 268-271°C.

Mixed m.p. with original acid (m.p. 270-273°C.) is 269-272°C.

70% of the starting material was recovered.

(2) The dibasic acid was dissolved in sulphuric acid (50% by volume) and this left standing for 12 hours. On pouring onto ice, a clear solution was still obtained and extraction of this solution with ether produced nothing in the ether layer. It was therefore concluded that sulphonation had taken place. Several experiments on the above lines with varying strengths of/

of sulphuric acid and varying reaction times proved equally unsuccessful in these cyclisation attempts.

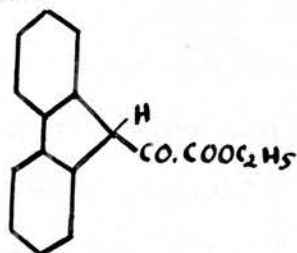
(3) The acid (1 g.) was refluxed with acetic anhydride (15 ml.) and glacial acetic acid (15 ml.) containing anhydrous zinc chloride (20 mg. per ml.) for 1 hour. This was then poured into water and extracted with ether. The ether layer was washed with water, extracted with sodium hydroxide solution, and then washed with water. After drying over anhydrous sodium sulphate the ether solution on evaporation yielded nothing. On acidification with concentrated hydrochloric acid the alkaline extractions and washings gave a white precipitate which on crystallisation from ethanol gave a white crystalline solid, m.p. 269-272°C.

Mixed m.p. with the original acid (m.p. 270-273°C.) was 270-273°C.

Yield of starting material = 90%.

Preparation of ethyl 1-keto-1'-(9-fluorenyl)-acetate.

cf. Wislicenus (Ber., 1900, 33, 771)
Thiele (Ibid. 852)



Thiele using the Wislicenus method obtained this/

this compound in good yield by boiling up equivalent quantities of fluorene, diethyl oxalate and sodium ethoxide in ethanol, and recrystallising the product from glacial acetic acid.

Fluorene (8.3 g., 0.05 mol.), diethyl oxalate (7.5 ml.) and sodium methoxide (2.9 g.) were refluxed in absolute ethanol (80 ml.) for 3 hours^{and} the product separated. Recrystallisation from glacial acetic acid gave an oil which solidified overnight, m.p. 68-74°C. This was crystallised from benzene (1 part) and light petroleum (2 parts) when yellow needles were obtained.

Yield = 40%

M.p. = 73-79°C. (Lit. 74-76°C.)

This method of Wislicenus proved unsatisfactory due to the large range in melting-point and the tendency of the crystallised product to revert to a liquid state, so the method of Kuhn and Levy who use the methyl ester was investigated.

Preparation of methyl 1-keto-1'-(9-fluorenyl)-acetate.

cf. Kuhn and Levy (Ber., 1928, 41, 2243)

Dimethyl oxalate (12 g.) was dissolved in absolute methanol (38 ml.) and a solution of potassium methoxide (from 4 g. potassium). Fluorene (13 g.) in pure dry ether (100 ml.) was added to the solution and/

and the mixture refluxed on a water-bath for 1 hour. The solution was then shaken with twice its volume of water to remove the compound which was present as the potassium salt of the enolic form. The ether solution was washed with dilute potassium hydroxide to remove any further quantities of the compound. The combined aqueous alkaline extracts were shaken with fresh ether to remove any dissolved fluorene and then acidified with 10% hydrochloric acid. After a few hours a yellow crystalline compound separated. This separated from glacial acetic acid in yellow needles.

Yield = 11.6 g. (58.5%)

M.p. = 125-127°C. (Lit. 117.5°C.
uncorrected)

Analysis: Found: C, 75.61%; H, 4.71%.

Calc. for $C_{18}H_{12}O_3$: C, 76.17%; H, 4.80%.

Preparation of 9-methyl fluorene.

Attempted condensation of the above compound with methyl iodide.

cf. Wislicenus and Densch (Ber., 1902, 35, 762)

Equimolecular quantities of the methyl 1-keto-1'-(9-fluorenyl)-acetate, methyl iodide and potassium were refluxed in absolute ethanol for 3 hours. On pouring the cooled solution into water no precipitate occurred, but on acidification with hydrochloric acid the/

the starting material was obtained in almost 100% yield.

Attempted Condensation of methyl 1-keto-1'-(9-fluorenyl) acetate with acrylonitrile.

The above substance (3.5 g., 0.14 mol.) was dissolved in dioxan (10 ml.) and acrylonitrile (2 ml.) and catalyst solution (5 ml.) added. The solution was placed in a water bath at 60° for two and a half hours, after no heating occurred on the addition of the reagents. It was then poured into acidulated water and this extracted with ether. The ether layer was washed with water, dried over anhydrous sodium sulphate, and then the ether evaporated off, when an orange-yellow oil was obtained. This was dissolved in benzene, which on the addition of light petroleum (b.p. 40-60°) gave a yellow crystalline precipitate. This crystallised from benzene in yellow needles.

M.p. = 124-126°C.

Mixed m.p. with original substance (m.p. 125-127°C.) is 125-127°C.

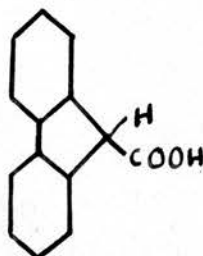
Various other attempts at this condensation were made under varying conditions of temperature and varying amounts of catalyst solution, but all proved equally unsuccessful.

Preparation/

Preparation of fluorene-9-carboxylic acid.

cf. Weissberger (Ber., 1908, 41, 2913)

Powdered sodamide (3 g.,
0.075 mol.) was stirred in small
quantities into a melt of
fluorene (12 g., 0.07 mol.)



maintained at 120°C. in an oil bath. Ammonia was evolved, and when the addition of sodamide was completed the temperature of the melt was raised to 150°C. where it was kept. The melt was cooled and the resulting orange brown mass, which contains sodium fluorene (one of the hydrogen atoms in the 9-position being substituted with sodium) was powdered and partially dissolved in benzene (200 ml., dried over sodium). An orange solution with a brown sediment resulted and to this was added carbon dioxide so that an evolution of carbon dioxide passed through the solid and liquid phases for one hour. With this treatment the solution cooled and went semi-solid, but ether (dried over sodium) was added to keep a liquid solution. The mixture was then set aside for 2 hours, till it attained room temperature, when it was shaken several times with sodium hydroxide solution. The dried (over anhydrous sodium sulphate) solution was evaporated to dryness, and the resulting red solid, on several crystallisations from benzene, yielded/

yielded 8.5 g. of white plates.

M.p. = 115-116°C.

Mixed m.p. with fluorene (m.p. 116°C.) is 115-116°C.

The sodium hydroxide extract was shaken with ether to clear the solution, and on acidification with concentrated hydrochloric acid a reddish solid was obtained which crystallised from glacial acetic acid. Discoloured white solid, m.p. 223-227°C.

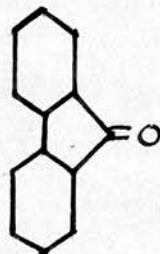
Yield = .75 g. (8%)

Recrystallisation from benzene gave elongated prisms, m.p. 229-232°C. (Lit. for fluorene-9-carboxylic acid, m.p. 230-232°C.).

Preparation of 9-fluorenone.

The method used was that described by Huntress, Hersberg and Cliff (J.A.C.S., 1937, 53, 2720).

To a refluxing solution of technical fluorene (100 g.) in glacial acetic acid (200 ml.) was added a hot solution of



sodium dichromate (300 g.) in a mixture of glacial acetic acid (400 ml.) and water (100 ml.) in a slow steady stream, so that boiling was not interrupted and no precipitation occurred. When all the oxidising solution had been added, refluxing was continued for two and a half hours. The now deep green solution was poured/

poured into 2 litres of ice-water and allowed to stand for at least 2 hours. The precipitate was filtered, and left to dry at the pump overnight, after washing with a little sulphuric acid and with water till all chromic acid had been washed out. The air dried fluorenone was then distilled in vacuo, the distillation being stopped, when the pale yellow liquid becomes orange. The pale yellow liquid solidified on cooling to a yellow crystalline mass which is 9-fluorenone.

M.p. = 81-83°C. (Lit. 84°C.)

Yield = 87 g. (80%)



Attempted preparation of 9-fluorenol.

Werner and Grab (Ber., 1904, 30, 2896) give the details for the preparation of 9-fluorenol from 9-fluorenone as follows.

Fluorenone (20 g.) is dissolved in alcohol (50 ml.) and concentrated ammonium hydroxide solution (500 ml.) is added. This solution is refluxed while ammonia/

ammonia is passed through the solution. An excess of zinc (35 g.) is added and after 2 hours when the reaction is complete the excess zinc is filtered and the 9-fluorenol allowed to crystallise from the hot solution.

This experiment was repeated, but the 9-fluorenone did not remain in solution, but was present as a suspension in the refluxing mixture. On adding the zinc the reactants went brown, and after one and a half hours became colourless when a greyish white precipitate was present. The solution was allowed to cool and the solid filtered. The white solid was dissolved from the excess zinc with hot ethanol, and the ethanolic solution filtered, the clear solution giving a white felt of needles on cooling.

Yield = 1 g.

M.p. = 149-152°C. (Lit. 153°C.)

An addition of water to the filtrate a further yield of pure white solid was obtained.

Yield = 12 g.

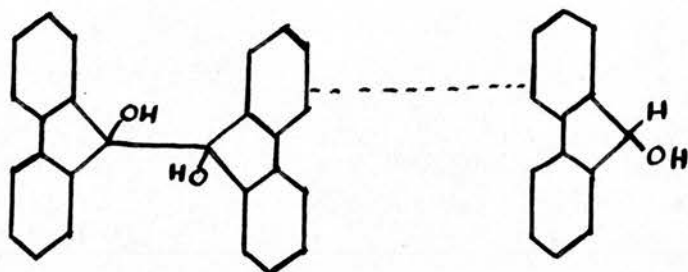
M.p. = 145-148°C.

Total yield = 19 g. (95%).

However a mixed m.p. with an authentic sample of 9-fluorenol (prepared by reduction of fluorenone with sodium in alcohol) was 130-137°C.

Therefore this compound could not be 9-fluorenol but was/

was probably the molecular mixture of fluorenol and fluorenopinacol obtained by Bachman (J.A.C.S., 1933, 55, 1185).



This same compound was obtained when zinc was added to a stirred suspension of fluorenone in a mixture of alcohol and ammonium hydroxide.

On modifying the procedure 9-fluorenol was obtained.

Fluorenone (20 g.) was dissolved in ethanol (100 ml.) and concentrated ammonia (100 ml.) added. This solution was refluxed while ammonia was passed through. Zinc dust (35 g.) was added in portions (7 g.) at 15 minute intervals and the solution which first turned brown became, after one and a half hours, practically colourless, and a white precipitate began to separate out on the sides of the ammonia inlet tube. Refluxing was continued for another thirty minutes when the solution was filtered free from zinc. On cooling a felt of needles separated out and this was filtered.

Yield/

Yield = 12 g.

M.p. = 150-153°C. (Lit. 153°C.)

Mixed m.p. with 9-fluorenol (authentic) = 151-153°C.

A further yield of 9-fluorenol was obtained by adding the filtrate to one litre of water when a gelatinous precipitate appeared.

Yield = 7 g.

M.p. = 144-147°C.

Crystallised from benzene this gave 5.5 g. of m.p. 149-151°C.

Total yield of 9-fluorenol = 17.5 g. (87%)

Preparation of 9-chlorofluorene.

cf. Schlenk and Bergmann (Ann., 1928, 463, 172)

Fluorenol (12 g.) was dissolved in methanol (70 ml.) and the solution saturated with hydrogen chloride. On standing this solution deposited long white needles of 9-chlorofluorene.

Yield = 8.4 g. (63%)

M.p. = 84-87°C.

Recrystallisation from methanol gave long needles, m.p. 91-92°C. (Lit. 92°C.).

Preparation/

Preparation of 9-ethylfluorene.

cf. Miller and Bachmann (J.A.C.S., 1935, 57, 771)

Ethyl iodide (7.8 g., 0.05 mol.) was made into a Grignard reagent in ether (50 ml.) and 9-chloro-fluorene (5 g., 0.025 mol.) added. The solution was refluxed for one hour, when the white precipitate formed had ceased to increase in bulk. Water, ice and dilute hydrochloric acid were added and the mixture filtered from bisdiphenylenethane.

Yield = 2.8 g. (56%)

M.p. = 243-244°C. (Lit. 244-245°C.)

The ether solution was separated, washed with water, and after drying over anhydrous sodium sulphate was evaporated to a light yellow oil, which could not be crystallised and which was 9-ethylfluorene.

Yield = 1.9 g. (28%)

Attempted condensation of the above product with acrylonitrile.

The 9-ethylfluorene (1.8 g., 0.01 mol.) was dissolved in dioxan (10 ml.) and the temperature raised to 25°C. The trimethylbenzylammonium hydroxide solution (1 ml.) was added and acrylonitrile (0.53 g., 0.1 ml.) added. No raising of temperature followed this addition, showing that no reaction had taken place.

Attempted/

Attempted condensation of 9-chlorofluorene with acrylonitrile.

This compound (2.00 g., 0.1 mol.) was dissolved in dioxan (10 ml.) and the trimethylbenzylammonium hydroxide solution added. On addition of acrylonitrile (0.53 g., 0.1 mol.) to the solution at 25°C. no rise in temperature took place. This was indicative of no reaction having taken place. This fact was confirmed as on addition of water to the dioxan a white solid was obtained which on crystallisation from methanol gave white needles of 9-chlorofluorene.

Yield = 1.5 g.

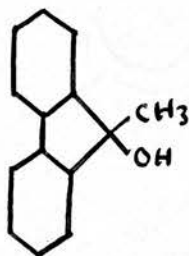
M.p. = 88-90°C.

Mixed m.p. with 9-chlorofluorene (m.p. 91-92°C.) was 89-91°C.

Preparation of 9-methylfluorenol.

cf. Daufresne (Bl., 4, 1, 1234)

Magnesium (2 g.) was made into a Grignard reagent with methyl iodide (15 g.) in presence of anhydrous ether (50 ml.). Fluorenone (12 g.) in anhydrous ether (125 ml.) was added slowly when a green unstable compound was obtained. When the addition was completed the mixture was heated on a water/



water-bath for 20 mins. The compound was decomposed on ice and dilute hydrochloric acid, when the product was taken up in the ether. The ether solution was washed with sodium bisulphite solution to rid it of liberated iodine, and was then washed with sodium bicarbonate solution and finally with water. After drying over anhydrous sodium sulphate the ether solution was evaporated to leave a white solid, which was crystallised from benzene.

Yield = 8 g.

M.p. = 172-173°C. (Lit. 173°C.)

Analysis: Found (1) C, 84.48; H, 5.8%.
(2) C, 86.39%; H, 6.18%.

Calc. for $C_{14}H_{12}O$: C, 85.63%; H, 6.16%.

Attempted reduction of 9-methylfluorenol to 9-methylfluorene.

Cf. Wanscheidt and Moldavski (Ber., 64, 917.

9-Methyl fluorenol (0.5 g.) was dissolved in glacial acetic acid (5 ml.) and hydriodic acid (1 ml.,

902) added, and this mixture boiled for 1 minute when sufficient of a solution of stannous chloride in fuming hydrochloric acid to turn the solution yellow was added. An oily precipitate which went solid on cooling was obtained. This experiment was repeated/

repeated several times and the products had a melting-point varying between 80-100° and 120-130°C.

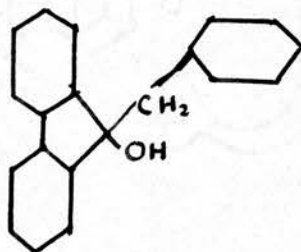
9-methylfluorene has m.p. 46°C.

Other attempts at this reduction were:

- (1) Dissolving the 9-methylfluorenol in alcohol and heating the solution with sodium. The original starting material was obtained.
- (2) Dissolving it in glacial acetic acid and refluxing with zinc dust when the product was again the original starting material.
- (3) Refluxing with phosphorus and hydriodic acid when the product had the m.p. 110-120°C.

Preparation of 9-benzylfluorenol.

Magnesium (2 g.) was made into a Grignard reagent with benzyl chloride (10 ml.) in anhydrous ether (50 ml.).



After some time the formation of Grignard reagent stopped due to deposition on the magnesium surface so that much of the magnesium remained unconverted.

Fluorenone/

Fluorenone (10 g.) was then added and on complete addition, the solution was refluxed for one hour. The compound formed was decomposed on ice and dilute hydrochloric acid. The ether layer was separated, dried (over anhydrous sodium sulphate) and evaporated down until a solution of the compound in the excess benzyl chloride was obtained. To this was added twice its volume of hot light petroleum (b.p. 60-80°) and the solution set aside, and from it was obtained white crystals of 9-benzyl fluorene, m.p. 137-139°C. (Lit. 139°C.).

Yield = 4 g. (26%)

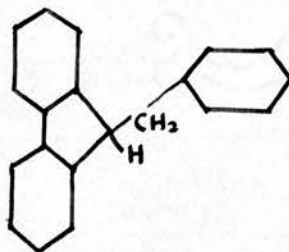
Analysis: Found: C, 87.43%; H, 5.93%.

Calc. for $C_{20}H_{16}$: C, 88.2%; H, 5.92%.

Reduction of 9-benzylfluorene to 9-benzylfluorene.

cf. Wanscheidt and Moldavski (Ber., 64, 917).

9-Benzylfluorene (3.5 g.) was dissolved in glacial acetic acid (35 ml.) and hydriodic acid (7 ml., $p = 1.90$) added, and the mixture heated to boiling for a few minutes, and a saturated solution of stannous chloride in fuming hydrochloric acid added till solution was yellow, when a white precipitate appeared. It was filtered after cooling and crystallisation from glacial acetic acid yielded white crystalline solid/



solid which was 9-benzylfluorene.

Yield = 2.8 g. (86%)

M.p. = 131-133°C. (Lit. 134°C.)

Mixed m.p. with 9-benzylfluorenol = 110-118°C.

Analysis: Found: C, 92.73%; H, 6.61%.

Calc. for $C_{20}H_{16}$: C, 93.74%; H, 6.26%.

Attempted condensation of 9-benzylfluorene with acrylonitrile.

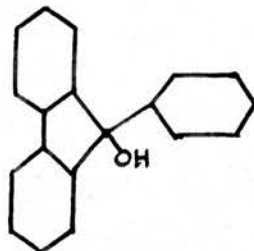
Several experiments were attempted to effect the condensation, using varying proportions of 9-benzylfluorene and acrylonitrile, using various quantities of the catalyst under varying conditions of temperature in both dioxan and benzene, but all these proved equally unsuccessful, the 9-benzylfluorene being recovered almost quantitatively in a fairly pure state.

Preparation of 9-phenylfluorenol.

cf. Ullman and von Wursterberger (Ber., 1904, 37, 13)

Magnesium (2 g.) was made into a Grignard reagent with bromobenzene (17.4 g.) in ether (35 ml.) dried over sodium) and fluorenone (10 g.)

was added in small portions with shaking after each addition. The mixture was then refluxed on a water-bath/



bath, when the initially green solution deposited a white solid. The cooled contents of the flask were poured on to ice and dilute hydrochloric acid to effect the decomposition of the Grignard compound and the product taken up in ether. The dried (over anhydrous sodium sulphate) ether solution was evaporated down to 20 ml. and light petroleum (4 ml., B.P. 60-80°) was added. White prisms crystallised from this.

Yield = 9 g. (87%)

M.p. = 66-67°C. (Lit. 106-107°C.)

This compound gave a characteristic colour reaction with concentrated sulphuric acid, and with concentrated sulphuric and glacial acetic acids. Also the melting-point of 9-phenylfluorenol is quoted as varying with the solvent from which it is crystallised (from carbon tetrachloride, m.p. is approximately 75°C. and benzene also gives a 'queer' melting-point) and since excess bromobenzene is present this may account for the low melting-point. Taking these things into consideration and the fact that it is unlikely that anything but 9-phenylfluorenol was formed, it was taken that the product was essentially pure. This hypothesis was found to be correct by subsequent reactions.

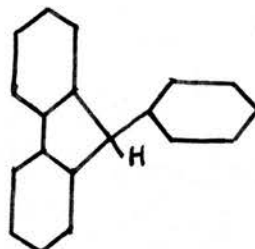
Reduction/

Reduction of 9-phenylCfluorenol to 9-phenylCfluorene.

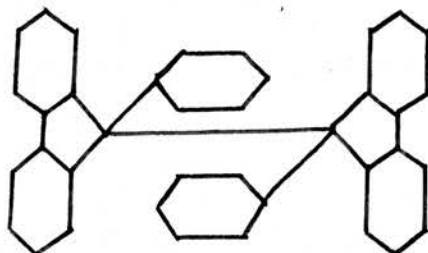
cf. Wanscheidt and Moldavski (Ber., 64, 917).

9-PhenylCfluorenol

(6 g.) was dissolved in glacial acetic acid (60 ml.) and hydriodic acid (12 ml., $p = 1.902$) was added, when a white



precipitate came down as the solution darkened in colour due to the formation of iodine. The solution was heated to boiling when the solid completely dissolves after a few minutes. (The solid which separates out was probably the dicondensation product diphenyl-bis-diphenylene ethane which is formed if excess hydriodic acid is not used).



A solution of stannous chloride in fuming hydrochloric acid was then added to the slightly cooled solution, until the solution was just yellow when the iodine formed in the reaction had been decolorised. White plates began to separate out and on dilution with water, the solution becomes colourless, and the 9-phenylCfluorene was obtained as white flat needles.

Yield/

Yield = 5.1 g. (90.5%)

M.p. = 145-146°C. (Lit. 146 or 148°C.)

This product also gave the blue fluorescence characteristic of 9-phenylfluorene in benzene and alcohol solutions.

Condensation of 9-phenylfluorene with acrylonitrile.

Method (1). In dioxan.

Acrylonitrile (2.5 ml.) was added drop by drop to a stirred solution of 9-phenylfluorene (5 g.) in dioxan (40 ml.) containing catalyst solution (0.5 ml.). Heating took place and temperature was kept below 35°. The solution became slightly brown and after the complete addition of the acrylonitrile it was allowed to stand for a further two hours at room temperature, when it was poured into water. The white solid precipitate was crystallised from glacial acetic acid.

Yield = 4.5 g. (73%)

M.p. = 146-148°C.

A sample crystallised from benzene, light petroleum mixture in elongated prisms, m.p. 148-149°C.

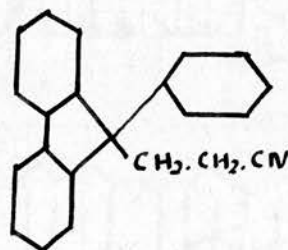
Mixed m.p. with 9-phenylfluorene is 120-125°C.

Thus/

Thus a condensation of monomolecular quantities of acrylonitrile and 9-phenylfluorene had taken place with the formation of 9-phenyl-9'-(2-cyanoethyl) fluorene or 3:3'-diphenylene-3''-phenylbutyronitrile.

Analysis: Found: N, 4.36%.

$C_{22}H_{17}N$ requires N, 4.73%.



Method (2) for benzene

Acrylonitrile (9 ml.) was added to a stirred solution of 9-phenylfluorene (17.5 g.) in benzene (200 ml.) containing the catalyst solution (1 ml.) at such a rate as to keep the temperature in the region of $40^{\circ}C$. When the addition of acrylonitrile was completed the now brown solution was set aside at room temperature for 2 hours. It was then heated to boiling and treated with charcoal, from which it was finally filtered. The almost colourless solution was reduced in volume by distillation to 25 ml., and boiling light petroleum (70 ml., b.p. $60-80^{\circ}$) added. On cooling the product crystallised out in prisms.

Yield/

Yield = 18.5 g. (86%)

M.p. = 145-148°C.

Mixed m.p. with 9-phenyl-9'-(2-cyanoethyl) fluorene is 146-149°C.

This product is pure enough for further reactions like hydrolysis.

Hydrolysis of 9-phenyl-9'-(2-cyanoethyl) fluorene.

9-Phenyl-9'-(2-cyanoethyl) fluorene (20) g.) was added to a mixture of ethanol (400 ml.) and water (200 ml.) containing sodium hydroxide (30 g.). The suspension formed was refluxed and after one hour a clear solution was obtained and ammonia was being evolved. The refluxing was continued for 10 hours when evolution of ammonia had ceased, and the brown solution was added to ice-water (1.5 litres) and set aside for 1 hour. The now turbid solution was filtered to clear and was then boiled with charcoal for a few minutes and filtered. The now almost colourless solution was acidified with concentrated hydrochloric acid and the solution set aside to cool. The precipitated white solid was filtered.

Yield = 20 g. (94%)

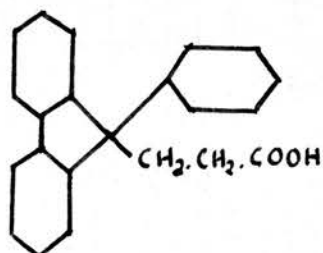
M.p. = 155-158°C.

The/

The product crystallised in white plates from aqueous ethanol (m.p. 159-160°C.) and was 9-phenyl-9'-(carboxyethyl)-fluorene or 3-phenyl-3:3'-diphenylene butyric acid.

Analysis: Found: C, 82.57%; H, 6.04%.

$C_{22}H_{18}O_2$ requires C, 84.02%; H, 5.9%.



Methyl ester was prepared by the usual methods and was obtained as fine colourless needles from ethanol, m.p. 97-98°C.

Analysis: Found: C, 84.2%; H, 6.38%.

$C_{25}H_{20}O_2$ requires C, 84.05%; H, 6.14%.

Cyclisation of 9-phenyl-9'-(2-carboxyethyl) fluorene.

The acid (1.5 g.) was converted to the acid chloride by refluxing with thionyl chloride (3 ml.) on a water-bath for 30 mins., the excess thionyl chloride being removed under reduced pressure at 50°C. The last traces of thionyl chloride were removed by taking off added light petroleum (5 ml., b.p. 100-120°) under reduced pressure, when a brown oil was left/

left and this was mainly the acid chloride. Light petroleum (7 ml., b.p. 100-120°) was then added and to the solution formed, anhydrous aluminium chloride is added in small quantities while it is heated on a steam bath. Heating was continued for 1 hour after the complete addition, and the brown mixture was extracted with ether and caustic soda. After separating the ether layer was washed and dried over anhydrous sodium sulphate. On evaporating off the ether a brown mass was obtained, which gave a positive dinitrophenylhydrazine test and is therefore ketone bearing.

Yield = 0.72 g.

Acidification of the sodium hydroxide extract yielded 0.4 g. of the original acid.

The ketone bearing oil was chromatographed in benzene through an alumina column (15" x 1").

(1) First 50 ml. collected gave a small amount of oil.

75 ml. gave a brown oil almost solid.

Crystallised from benzene/light petroleum,
m.p. 143-147°C.

Two further crystallisations from
the same solvent, m.p. 147-149°C.

50 ml. slight amount of oil.

Alcohol extraction of column gives negligible amount of oil.

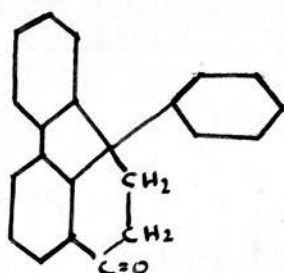
Yield/

Yield of solid ketone with respectable melting-point = 0.18 g.

Compound obtained was probably 4-keto-1-phenyl-1:2:3:4-tetrahydrofluoranthene.

Analysis: Found: C, 87.4%; H, 5.31%.

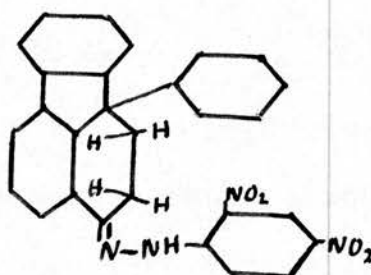
$C_{22}H_{17}O$ requires C, 88.8%; H, 5.76%.



A sample of the solid ketone (0.08 g.) was converted into the 2:4-dinitrophenyl hydrazone by dissolving it in ethanol (2 ml.) and adding a suspension of the reagent (2 ml.) in ethanol and heating to boiling. Concentrated hydrochloric acid (2 drops) was added and a red precipitate was obtained. On boiling with glacial acetic acid (5 ml.) most of the dinitrophenylhydrazone did not dissolve. On filtering hot, orange needles were obtained, m.p. 302-303°C. These were the dinitrophenylhydrazone of 4-keto-2-phenyl-1:2:3:4-tetrahydrofluoranthene.

Analysis: Found: N, 11.7%.

$C_{22}H_{15}N_2O_4$ requires N, 11.73%.



Condensation of acrylonitrile with 9-fluorenone.

9-Fluorenone (6 g.) was dissolved in dioxan (30 ml.) and trimethylbenzylammonium hydroxide (1 ml.) added. Acrylonitrile (3 ml.) was added drop by drop to the stirred solution so that the temperature was kept between 30 and 40°C. Stirring was continued for 1 hour, and the crude solution left at room temperature for 2 hours, when it was poured into water (80 ml.). The resulting yellow oil was taken up in ether, and the ether layer after several washings with water and drying over calcium chloride was evaporated. The resulting yellow oil (6.6 g.) was dissolved in benzene, and light petroleum (B.P. 60-80°C.) added to the hot solution. An oily layer was obtained on cooling, which after several days deposited a white crystalline mass.

Yield = 1.1 g.

M.p. = 102-106°C.

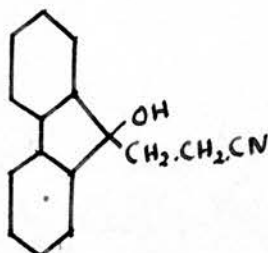
The solid was recrystallised with difficulty from a benzene/light petroleum mixture, and from aqueous methanol, great care being essential as the solid tended to revert to an oil.

M.p. of white prisms from aqueous methanol = 105-107°C.
Analysis indicated that this compound was 3:3'-di-phenylene-3"-hydroxybutyronitrile.

Analysis/

Analysis: Found: C, 81.34%; H, 5.79%; N, 5.89%.

$C_{16}H_{13}ON$ requires C, 81.66%; H, 5.57%; N, 5.95%.



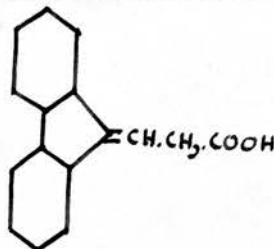
The yellow oil was recovered from the benzene light petroleum mixture by evaporation of the solvents, but decomposed on an attempted vacuum distillation.

Properties of the oil obtained from the condensation of acrylonitrile with 9-fluorenol.

(1) Hydrolysis with sodium hydroxide solution.

Preparation of 3:3'-diphenylenevinylacetic acid.

The yellow oil (20.3 g. from 18.2 g. fluorenol was refluxed for 5 hours with sodium hydroxide (8 g. NaOH in 200 ml. water) and



ammonia was given off. The slightly turbid brown solution was diluted to 400 ml. and when cool was filtered to clear the solution, 1.5 g. of a solid being obtained. This crystallised from benzene light/

light petroleum. M.p. = 148-151°C.

Mixed m.p. with 9-fluorenol (m.p. 152-153°C.) was 149-151°C.

The filtrate was heated to 60°C. and acidified with concentrated hydrochloric acid, when a brownish semi-solid was precipitated. This was dried, dissolved in 280 ml. benzene and 280 ml. light petroleum (B.P. 100-120°C.) added. On cooling white elongated prisms were obtained.

Yield = 9.1 g.

M.p. = 134-136°C.

Several crystallisations from benzene/light petroleum gave colourless elongated prisms, m.p. 136-137°C.

A further yield of the compound was obtained by evaporating the mother liquor to 50 ml. On cooling this gave a sticky brown solid which after extraction with light petroleum (B.P. 100-120°C.) (4 portions of 50 ml.) gave only a small quantity of a light brown oil. The extracts on cooling deposited white broad needles.

Yield = 3.6 g.

M.p. = 129-132°C.

Mixed m.p. with the compound obtained above was 131-134°C.
Total yield of 3:3'-diphenylenevinylacetic acid = 12.7 g. (53.8%).

Analysis/

Analysis: Found: C, 80.81%; H, 4.85%.

$C_{16}H_{12}O_2$ requires C, 81.4%; H, 5.1%.

(2) The yellow oil (5 g.) was refluxed with concentrated hydrochloric acid (150 ml.) and water (150 ml.) for one and a half hours, the resulting oil taken up in ether, and the ether layer washed with water and dried over anhydrous sodium sulphate. On evaporation a brown solid was obtained. This was extracted with light petroleum (B.P. 100-120°C.) leaving a brown solid, and the cooled extracts deposited white needles tinged with orange.

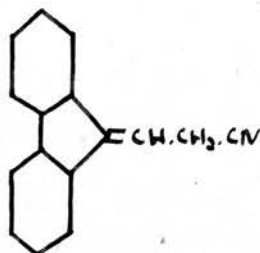
Yield = 1.3 g. (26%).

M.p. = 95-98°C.

These were extracted with light petroleum (80-100°C.) leaving a small quantity of red oil and the extract deposited long fine white needles, m.p. 100-101°C. This compound was 3:3'-diphenylenevinylacetonitrile.

Analysis: Found: C, 87.36%; H, 5.14%; N, 6.73%.

$C_{16}H_{11}N$ requires C, 88.4%; H, 5.15%; N, 6.45%.



The residue from the initial extractions crystallised from benzene in a felt of white needles.

Yield = 1.9 g. (37%)

M.p. = 197-199°C.

Mixed/

Mixed m.p. with 3:3'-diphenylenebutyro- γ -lactone (m.p. 200-201°C.) (p. 66) was 199-200°C.

(3) The oil was acted on with Grignard reagents by refluxing in dried ether solution with mono-molecular proportions of (i) phenyl magnesium bromide and (ii) methyl magnesium iodide for 6 hours on a steam bath. The resulting white precipitates were decomposed on equal amounts of ice and hydrochloric acid, the ether removed by distillation, and the residual oil refluxed with the hydrochloric acid for one hour. The resulting oil was taken up in ether, the ether layer washed with water, dried over anhydrous sodium sulphate and evaporated to yield a brown solid which was found to be of similar composition to that obtained in (2) above. It was therefore concluded that no reaction had taken place between the nitrile and the Grignard reagent.

Properties of 3:3'-diphenylene-3"-hydroxybutyronitrile.

(1) The nitrile (0.2 g.) was refluxed with concentrated hydrochloric acid (5 ml.) and water (5 ml.) for 30 min. during which time the solid melted and became almost black in colour. After cooling the oil was extracted with ether. The ether layer was washed with water, dried over anhydrous sodium sulphate, and evaporated to yield a dark brown oil which solidified on/

on cooling. Extraction with light petroleum (B.P. 80-100°C.) left a small amount of oil and on cooling the solution deposited pinkish white needles.

M.P. = 97-98°C.

Yield = 0.14 g.

Mixed m.p. with 3:3'-diphenylenevinylacetonitrile (p. 59) of m.p. 100-101°C. was 98-100°C.

(2) The nitrile (0.2 g.) was refluxed with sodium hydroxide solution (10%) for one and a half hours when evolution of ammonia had ceased. The solution was filtered and acidified with concentrated hydrochloric acid to give a white precipitate.

Yield = 0.15 g.

This crystallised from benzene/light petroleum in long needles, m.p. 130-131°C.

Mixed m.p. with 3:3'-diphenylenevinylacetic acid (p. 57) of m.p. 136-137°C. was 132-135°C.

Properties of 3:3'-diphenylenevinylacetonitrile.

(1) The nitrile (0.2 g.) was refluxed in a solution of glacial acetic acid (10 ml.) and hydrobromic acid (10 ml. of 34%) for 1 hour. On cooling and adding water a white precipitate was obtained which after drying crystallised from benzene in a felt of needles.

Yield = 0.16 g.

M.p. = 198-200°C.

Mixed/

Mixed m.p. with 3:3'-diphenylenebutyro- γ -lactone (p. 66) of m.p. 200-201°C. was 199-200°C.

(2) The nitrile was refluxed in concentrated hydrochloric acid (10 ml.) and water (10 ml.) for 1 hour. On cooling a dark brown solid was obtained, which crystallised from benzene in a felt of discoloured white needles.

Yield = 0.11 g.

M.p. = 195-197°C.

Mixed m.p. with 3:3'-diphenylenebutyro- γ -lactone (p. 66) of m.p. 200-201°C. was 198-200°C.

(3) The nitrile (0.5 g.) was dissolved in dried ether (50 ml.) and added to a solution of the Grignard reagent made from magnesium (0.06 g.) and methyl iodide (0.36 g.) in dried ether (10 ml.) and the resulting solution and white solid precipitate refluxed for 2 hours. Ice (10 g.) and concentrated hydrochloric acid (10 ml.) were then added, the ether removed by distillation, and the residue refluxed for 15 min. The oily layer in the hydrochloric acid went solid on cooling in ice water. It was filtered, dried and extracted with light petroleum (B.P. 80-100°C.) to leave a small quantity of oil, the solution depositing white needles with a red tinge.

Yield = 0.38 g.

M.p. = 97-99°C.

Mixed/

Mixed m.p. with original nitrile (m.p. 100-101°C.) was 98-100°C.

(4) The nitrile (0.5 g.) was refluxed with sodium hydroxide solution (20 ml. of 10%) for 30 hours when ammonia was still being evolved and a white sublimate had formed in the condenser.

Yield of sublimate = 0.14 g.

M.p. = 111-113°C.

Mixed m.p. with fluorene (m.p. 116°C.) = 112-114°C.

The sodium hydroxide solution was filtered free from a dark brown oil which went solid on cooling and was acidified. A small quantity of brown solid separated from which nothing could be extracted with light petroleum (B.P. 100-120°C.). The solid insoluble in the alkaline solution was also totally insoluble in light petroleum, but was soluble in benzene and alcohol, but no pure crystalline compound could be separated.

Bromination of 3:3'-diphenylenevinylacetic acid.

The acid (2.4 g., 0.01 mol.) was dissolved in the minimum of cold glacial acetic acid and bromine (1.6 g., 0.01 mol.) was added. After 3 hours the solution was practically free from bromine coloration. The brownish slightly sticky solid precipitated by water, was extracted with hot light petroleum (B.P. 100-120°C.). On cooling the solution a white solid was/

was deposited.

Yield = 1.5 g.

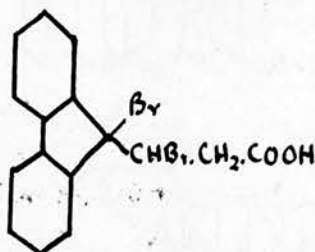
M.p. = 154-158°C.

Crystallisation twice from benzene resulted in colourless elongated prisms, m.p. 166-167°C.

This compound was 2:3-dibromo-3':3''-diphenylene-butyrlic acid.

Analysis: Found: Br, 40.74%.

$C_{16}H_{12}O_2Br_2$ requires Br, 40.34%.



The uncrystallised dibromo compound obtained above was dissolved in glacial acetic acid (10 ml.) and this solution refluxed with zinc dust (5 g.) for 15 min. After filtering free from zinc, a white compound was precipitated by water and crystallised from benzene. M.p. 186-190°C.

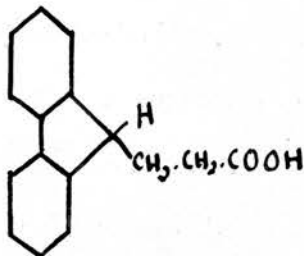
Further crystallisation from benzene gave white needles (m.p. 197-199°C.) which gave a blue fluorescence in ultraviolet light.

Mixed m.p. with 3:3'-diphenylenebutyro- γ -lactone (m.p. 200-201°C.) (p. 66) was 198-200°C.

Yield = 41% of pure lactone.

Reduction/

Reduction of 3:3'-diphenylenevinylacetic acid to 9-fluorenyl-2-propionic acid.



Method (1). Catalytic hydrogenation. The catalyst used was brown platinum oxide, which was prepared as in Organic Synthesis, VIII, p. 92.

3:3'-Diphenylenevinylacetic acid (2.4 g.) was dissolved in glacial acetic acid (100 ml.) in a pressure bottle and the catalyst (0.1 g.) added. The solution was then shaken in an atmosphere of hydrogen at 60 lbs. pressure, when the pressure fell 5 lbs. in 20 min. Air was then substituted for hydrogen and the contents shaken. Hydrogen at the same pressure was again introduced when no pressure drop occurred. A further portion of the catalyst was added (0.1 g.) and a pressure drop of 4 lbs. recorded. The volume of the acetic acid was reduced to 10 ml. by distillation and water added to precipitate a brownish sticky compound. This was extracted several times with light petroleum (B.P. 100-120°C.) until nothing further separated from the cooled extracts, when a small quantity of brown tar remained. Large flat white/

white needles were obtained.

Yield = 1.8 g.

M.p. = 134-138°C.

Several crystallisations from benzene gave white needles, m.p. 141-142°C. Yield = 50%.

Meyer (Ber., 1913, 46, 2579) quotes m.p. of 9-fluorenyl-2-propionic acid as 144°C. a/

Analysis: Found: C, 80.28%; H, 6.25%.

Calc. for $C_{16}H_{14}O_2$, C, 80.63%; H, 5.92%.

Method (2). This followed the method of H. Rupe and Steinbeck (Ber., 1911, 44, 584) for the saturation of β - γ -unsaturated bonds in carboxylic acids. ccl

This was a 2-stage process.

(1) Formation of 3:3'-diphenylenebutyro- γ -lactone.

The acid (8 g.) was refluxed with sulphuric acid (150 ml. of 10%) for two and a half hours, and the mixture poured onto ice water (150 ml.). The resulting white solid was filtered.

Yield = 7.7 g. (94%)

A sample crystallised from benzene in a felt of white needles which gave a blue fluorescence in ultraviolet light. M.p. = 200-201°C.

Analysis: Found: C, 80.17%; H, 5.0%.

$C_{16}H_{13}O_2$ requires C, 81.0%; H, 5.4%.

This/

This compound also gives a violet coloration when shaken with sodium hydroxide solution and a small crystal of sodium nitroprusside.

(2) Reduction of the lactone to 9:fluorenyl-2-propionic acid.

The lactone (7.5 g.) was refluxed for 5 hours with red phosphorus (6 g.), hydriodic acid (25 ml., $d = 1.9$) and water (10 ml.). The reaction mixture was added to water (50 ml.), allowed to cool, and extracted with ether. The ether layer was washed with sodium bicarbonate solution to neutralise any acid, then with sodium bisulphite solution to remove all iodine, and finally with sodium ^{bicarbonate} ~~bisulphite~~. The ether layer was extracted with sodium carbonate solution (50 ml. of 60% in 10 ml. portions). On acidification a brown sticky solid was obtained which was extracted five times with 30 ml. portions of light petroleum (B.P. 100-120°), leaving a small quantity of brown tar. On cooling the extractions yielded white flat needles.

Yield = 4.5 g. (60%)

M.p. = 139-141°C.

Colourless needles were obtained after two crystallisations from benzene. M.p. = 143-144°C, (Lit. 144°C.).

Mixed/

Mixed m.p. with compound obtained from catalytic hydrogenation (m.p. 141-142°C.) was 142-144°C.

Attempts were made to obtain the hydroxy acid from the 3:3'-diphenylenebutyro- γ -lactone, by dissolving it in hot sodium hydroxide solution, cooling and acidifying the resulting solution with hydrochloric acid, but in all attempts there was no immediate precipitation and the lactone slowly separated out.

Attempted cyclisation of 3:3'-diphenylenevinylacetic acid.

The acid (1 g.) was refluxed for 3 hours with acetic anhydride (5 ml.) containing sodium acetate (0.55 g.) and the cooled solution treated with water (100 ml.). A white precipitate was obtained.

Yield = 1 g.

M.p. = 133-135°C.

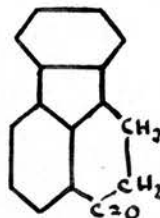
Mixed m.p. with 3:3'-diphenylenevinylacetic acid (m.p. 136-137°C.) was 134-136°C.

Synthesis/

Synthesis of fluoranthene from 9-fluorenyl-2-propionic acid.

(1) Cyclisation of the acid to 4-keto-1:2:3:4-tetrahydrofluoranthene.

The fluorenylpropionic acid (4.8 g., 0.02 mol.) was converted to the acid chloride by refluxing with thionyl chloride (8 ml.) on a water-bath for one hour, and then removing the excess thionyl chloride at 50°C. under reduced pressure. The last traces of thionyl chloride were removed by adding light petroleum (5 ml., B.P. 100-120°) and taking this off at 50°C. under reduced pressure. The brown oil obtained, being essentially the required acid chloride, was dissolved in light petroleum (25 ml., B.P. 100-120°) and this heated in a steam bath. Anhydrous aluminium chloride (3.2 g., 0.025 mol.) was then added in small portions over a period of 20 min. and heating was continued for a further one and a half hours. Sodium hydroxide solution (10%) was added to the cooled solution and this transferred to a separating funnel. The brown solid residue was alternately extracted with sodium hydroxide and ether (3 times with 20 ml. of each solvent) and the two layers separated. The sodium hydroxide solution was acidified and from the dirty brown/



brown precipitate some of the original acid was obtained after recrystallisation from benzene/light petroleum mixture.

Yield = 0.45 g.

The ether solution was washed with water, dilute acid and then with sodium bicarbonate solution. The dried (over anhydrous sodium sulphate) solution was evaporated to give a brown sticky oil.

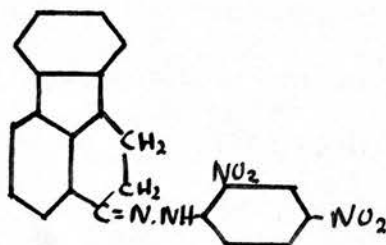
Yield = 3.3 g.

A sample of this oil (0.2 g.) was dissolved in alcohol (2 ml.) and a suspension of dinitrophenylhydrazine in alcohol (2 ml.) was added. This mixture was heated to boiling when concentrated hydrochloric acid (2 drops) was added, and on heating once more an orange precipitate appeared almost immediately.

Yield = 0.12 g.

M.p. = 231-234°C.

Crystallisation from glacial acetic acid gave m.p. 234-236°C. This was the dinitrophenylhydrazine of 4-keto-1:2:3:4-tetrahydrofluoranthene.



Analysis: Found: N, 13.7%.

$C_{22}H_{14}O_4N_4$ requires N, 13.96%.

The remainder of the brown oil was chromatographed. The oil was dissolved in benzene and introduced into a column of alumina (18" x 1"). Various bands were developed by means of a mixture of benzene (1 part) and light petroleum (1 part, B.P. 60-80°).

In the first 200 ml. run through the column a small quantity of oil was obtained but this was non-ketone bearing. (Test by adding a minute quantity of the oil to 1 ml. of dinitrophenylhydrazine solution and treating as above).

The third 100 ml. gave a slight amount of oil which gave a slight turbidity on testing for a ketone.

The fourth to seventh 100 ml. collected, corresponding to a band fluorescing bright blue in ultraviolet light gave a positive test for ketone.

M.p. of dinitrophenylhydrazine is 229-232°C.

Mixed m.p. with that obtained above is 231-234°C.

Yield of oil obtained was 1.8 g.

The next 100 ml. corresponding to a band with a greenish fluorescence yielded a brown oil which soon went solid. Yield = 0.2 g. This crystallised from benzene/light petroleum in yellow prisms/

prisms, m.p. 94-97°C. Von Braun gives for m.p. of 4-keto-1:2:3:4-tetrahydrofluoranthene 98°C.

Dinitrophenylhydrazine prepared m.p. = 234-236°C.

Mixed m.p. with those obtained above, m.p. = 234-236°C.

(2) Clemmensen reduction on the ketone bearing oil.

Zinc dust (15 g.) and mercuric chloride (1.5 g.) was shaken with water (20 ml.) and concentrated hydrochloric acid (0.75 ml.) for 5 min. when the zinc went into a solid mass. The aqueous solution was decanted and the zinc amalgam washed with water, which was removed by decantation. The ketone bearing oil (1.8 g.) in toluene (10 ml.) was added and the mixture thoroughly shaken. Concentrated hydrochloric acid (20 ml.) was then added and the mixture refluxed for 4 hours, during which time the toluene drops lost most of their brown colour. After cooling the liquid was decanted into a separating funnel. The zinc was then extracted 5 times with ether (15 ml.) and these extractions transferred to the separating funnel. After shaking, the acid layer was removed and the ether washed with water. The dried (over anhydrous sodium sulphate) ether solution, which gives a slight blue fluorescence in daylight and a bright blue fluorescence in ultraviolet light, was evaporated, yielding/

yielding an almost solid brown mass which contained 1:2:3:4-tetrahydrofluoranthene (see below).

Yield = 1.32 g.

A test for ketone, carried out on the oil with dinitrophenylhydrazine was negative.

Dehydrogenation of above oil and separation of fluoranthene.

The oil (1.32 g.) was dissolved in sulphur-free xylene (20 ml.) and to this was added chloranil (1.57 g.) and the mixture refluxed for 24 hours. The resulting mixture was decanted into a separating funnel and the solid left in the flask alternately extracted with sodium hydroxide solution and ether, and the extracts transferred to the separating funnel. The two layers were separated, the sodium hydroxide layer removing reduced chloranil. The dried (anhydrous sodium sulphate) ether layer was evaporated almost to dryness when a red tar was obtained. Trituration with alcohol removed an oil leaving a red solid which was unchanged chloranil. The red alcohol solution was reduced in volume to 3 ml., and a saturated picric acid solution (3 ml.) was added. On heating and allowing to cool this solution deposited orange yellow needles.

Yield = 0.15 g.

M.p. = 171-174°C.

Fluoranthene picrate was made from an authentic sample of fluoranthene.

M.p. = 179-181°C.

Mixed m.p. of picrate obtained with fluoranthene picrate is 176-178°C.

The above picrate was dissolved in ether, and the ether layer washed with sodium hydroxide solution until no yellow coloration was obtained in the alkaline layer, showing all the picric acid had been removed from the ether layer. The ether layer, which was pinkish with a slight blue fluorescence, and which fluoresced bright blue in ultraviolet light, was washed with water. After drying over anhydrous sodium sulphate the ether solution was evaporated to yield a white solid with a pinkish tinge. Crystallisation from benzene/light petroleum gave pink discoloured needles.

Yield = 0.06 g.

M.p. = 105-107°C. (Lit. for fluoranthene is 110°C.)

Mixed m.p. with authentic example of fluoranthene, 106-108°C.

Therefore fluoranthene has been synthesised from 9-fluorenyl-2-propionic acid in a yield of 1.5%.

Yield of fluoranthene from fluorene = 0.36%.

Preparation/

Preparation of Cinnamitrile (Styryl Cyanide).

(1) Preparation of cinnamamide from cinnamic acid.

Cinnamic acid (20 g.) was refluxed for one and a half hours on a water-bath with thionyl chloride (30 ml.). The excess thionyl chloride was distilled off under vacuum and when there was a decided rise in temperature during the distillation, the receiver was changed and the acid chloride distilled over. The acid chloride was dissolved in anhydrous ether dried over sodium (200 ml.) and ammonia from a cylinder passed into the solution. A white precipitate was formed which was filtered and washed with ether. Ammonia was passed into the filtrate and washings, and this process of filtering off solid washing with ether, and further passing in of ammonia, was carried on until no further precipitation occurred.

The ether solution was yellow and contained a small quantity of yellow oil which was not investigated. The white precipitate containing cinnamamide and ammonium chloride with a little unchanged cinnamic acid, was treated with boiling water (200 ml.) containing concentrated ammonium hydroxide (20 ml.). This dissolved out the ammonium chloride and cinnamic acid. Cinnamamide was filtered off, and the filtrate allowed to cool when a further yield of cinnamamide crystallised/

crystallised out. Undissolved portion was crystallised from aqueous alcohol.

Yield = 14.5 g. (72.5%).

M.p. = 144-146°C. (Lit. 148°C.).

(2) Preparation of cinnamnitrite from cinnamamide.

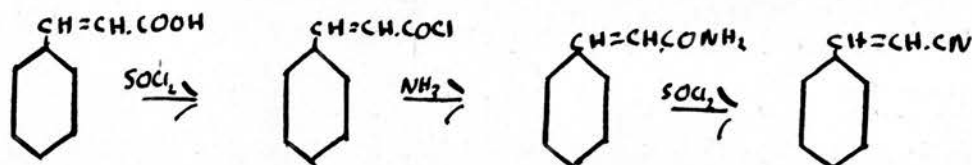
Cinnamamide (13 g.) was refluxed with thionyl chloride (20 ml.) for 1 hour on a steam-bath. The excess thionyl chloride was removed under reduced pressure and the main bulk of the remaining liquid distilled at 180-185°C. at 100 mm. This was a clear yellow liquid and distillation was stopped when a darker liquid, of which there was almost negligible quantity, appeared. The clear yellow liquid was dissolved in ether and shaken with potassium carbonate solution to free the cinnamnitrite from any adhering acids. The ether solution (dried over anhydrous potassium carbonate) was placed in a distilling flask, the ether removed under reduced pressure and the cinnamnitrite redistilled under vacuum.

B.P. 175°C. at 76 mm. (Lit. B.P. 255°C.
B.P. 134-136°C. at
13 mm.)

Yield = 7 g. (62%).

Equation/

Equations for complete reaction:



Condensation of cinnamitrile with fluorene.

(1) In dioxan.

Fluorene (5 g.) was heated with cinnamitrile (4.5 g.) in dioxan (35 ml.) containing the catalyst solution (1 ml.), in a steam-bath for three and a half hours, and the solution which first turned green and finally became purple tinted was poured into water when a solid separated. This was dissolved in hot alcohol and this treated with charcoal, and filtered. To the heated filtrate, hot water was added until precipitation almost occurred. On cooling 2-phenyl-2'-(9-fluorenyl) propionitrile crystallised out in colourless prisms.

Yield = 4.5 g. (50%).

M.p. = 147-149°C.

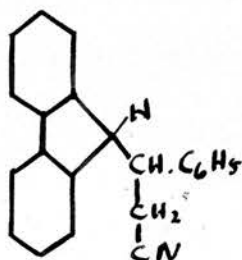
Sample crystallised twice from aqueous alcohol has m.p. 151-152°C.

Thus/

Thus was obtained 2-phenyl-2'-(9-fluorenyl) propionitrile.

Analysis: Found: N, 4.36%.

$C_{22}H_{17}$ requires N, 4.73%.



(2) In toluene.

Fluorene (5 g.) was dissolved in toluene (40 ml.) and to this was added cinnamnitrite (4.5 g.) and the catalyst solution (1 ml.). The solution was heated on the steam-bath for three and a half hours, the solution soon turning green and then becoming purple and depositing a slight sticky purple tar on the sides of the containing flask. After about 3 hours a further addition of the catalyst (1 ml.) was made. Toluene (20 ml.) was added to the solution and all raised to boiling, when it was treated with charcoal to remove tar. Boiling light petroleum (B.P. 60-80°) was stirred into the now pinkish clear solution, until precipitation almost occurred. On cooling white prisms crystallised out.

Yield /

Yield = 5.1 g. (57%)

M.p. = 148-149°C.

Mixed m.p. with 2-phenyl-2'-(9-fluorenyl)-propionitrile (m.p. 151-152°C.) is 149-151°C.

Hydrolysis of the above nitrile to 2-phenyl-2'-(9-fluorenyl) propionic acid.

2-Phenyl-2'-(9-fluorenyl) propionitrile (9 g.) was refluxed in a mixture of alcohol (200 ml.) and water (100 ml.) containing sodium hydroxide (15 g.) for 20 hours, the solution becoming clear after 4 hours, while ammonia was evolved. The solution was cooled and the white insoluble precipitate which appeared was filtered.

Yield = 2.7 g.

A sample crystallised from a mixture of benzene and light petroleum, m.p. 207-208°C.

This was proved to be 2-phenyl-2'-(9-fluorenyl) propionamide as mixed m.p. with this substance (m.p. 206-207°C.) was 207-208°C.

The alkaline solution was acidified with concentrated hydrochloric acid and a slightly brown solid was obtained.

Yield = 6.2 g.

M.p. = 175-178°C.

A/

A sample crystallised from aqueous alcohol

M.p. 181-182°C.

The alkaline insoluble portion (2 g.) was refluxed in alcohol (75 ml.) and water (100 ml.) containing sodium hydroxide (4 g.) for 30 hours when evolution of ammonia had completely ceased. On cooling a clear solution was obtained which on acidification gave a white compound.

Yield = 1.7 g.

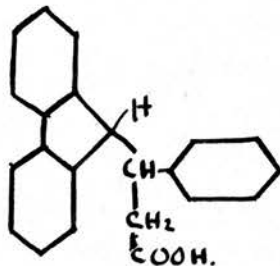
M.p. = 174-178°C.

Mixed m.p. with the acid obtained above (m.p. 181-182°C.) is 177-180°C.

Total yield of the 2-phenyl-2'-(9-fluorenyl) propionic acid is about 90%.

Analysis. Found: C, 84.28%; H, 5.93%.

$C_{22}H_{18}O_2$ requires C, 84.02%; H, 5.9%.



Preparation/

Preparation of the methyl ester of the above acid.

The acid (1 g.) was refluxed for 1 hour with methyl alcohol containing concentrated sulphuric acid (8 drops) and then added to water when the resulting oily precipitate was taken up in ether. The ether solution was shaken with potassium carbonate solution, dried over anhydrous sodium sulphate after washing with water, and then evaporated to dryness. The oil obtained after three crystallisations from benzene (1 part) and light petroleum (B.P. 40-60°)(3 parts) yielded a very small quantity of white crystals.

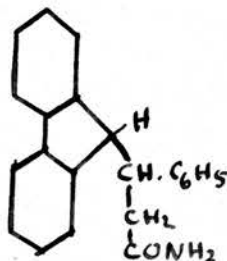
M.p. = 81-82°C.

Analysis. Found: C, 83.71; H, 6.42%.

$C_{23}H_{20}O_2$ requires C, 84.05; H, 6.14%.

Preparation of 2-phenyl-2'-(9-fluorenyl) propionamide.

The carboxylic acid obtained above (0.7 g.) was refluxed with thionyl chloride (2 ml.) on a steam-bath for 30 min. and then the excess



thionyl chloride removed under reduced pressure at 50°C. Anhydrous ether (20 ml.) was then added and ammonia from a cylinder passed through the solution and/

and in a few minutes a white precipitate formed which was filtered from the ether and washed with dilute ammonia.

Yield = 0.5 g.

M.p. = 201-204°C.

The white compound crystallised from alcohol in fine needles, m.p. = 206-207°C.

Analysis. Found: N, 4.33%.

$C_{22}H_{19}ON$ requires N, 4.51%.

Cyclisation of 2-phenyl-2'-(9-fluorenyl) propionic acid.

The acid (3.2 g.) was made into the acid chloride by treatment with thionyl chloride as detailed above. The resulting brown oil was taken up in light petroleum (20 ml., B.P. 100-120°) and anhydrous aluminium chloride was added in small portions to this solution heated in a steam bath, where it was heated for a further 2 hours. The ether and sodium hydroxide extracts of the products were separated, the ether layer washed with water, dried over anhydrous sodium sulphate and evaporated to yield a brown oil (2.4 g.) which gave a positive dinitrophenylhydrazine test and was therefore ketone bearing.

This/

This oil was dissolved in the minimum quantity of benzene and introduced into an alumina column (15" x 1") and bands were developed on the column with a mixture of benzene (4 parts) and light petroleum (B.P. 100-120°; 1 part). Two moving bands were obtained which gave a bright blue fluorescence in ultraviolet light.

The first yielded an oil (0.1 g.) in 50 ml. solvent and was non-ketone bearing.

An intermediate yellow band yielded an oil (0.3 g.) in 100 ml. solution and this was also non-ketone bearing.

The second band yielded an oil (1.3 g.) in 180 ml. solvent and this contained a ketone.

A dinitrophenylhydrazone was formed, m.p. 311-314°C. No further ketone bearing bands were obtained.

The ketone bearing oil was crystallised from benzene (3 ml.).

Yield = 0.9 g.

M.p. = 120-130°C.

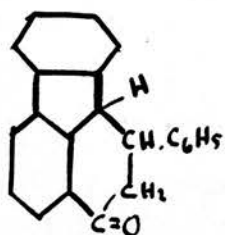
It was then crystallised from a benzene/light petroleum (B.P. 40-60°) mixture several times when the yield was greatly reduced, m.p. 167-168°C.

Compound was suspected of being 4-keto-2-phenyl-1:2:3:4-tetrahydrofluoranthene.

Analysis/

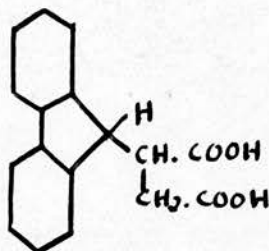
Analysis. Found: C, 86.4%; H, 5.45%.

$C_{22}H_{17}O$ requires C, 88.9%; H, 5.76%.



Preparation of 9-fluorenylsuccinic acid.

cf. Preparation of 9-fluorenylsuccinic anhydride by Vagt, Alder and Pascher (Ber., 1942, 75B, 1511).



Fluorene (16.5 g.) and maleic anhydride (10 g.) were heated together in a sealed tube for 16 hours at 250°C. The tube was opened, the glass smashed, and the brown sticky product extracted with hot sodium carbonate solution. A dark brown solution was obtained which left a residue, which dissolved in alcohol and was then precipitated by water to give a whitish solid.

Yield = 3.5 g.

M.p. = 110-112°C.

Mixed m.p. with fluorene (m.p. 116°) = 111-114°C.

Therefore it was fluorene.

The carbonate extract was acidified when a whitish brown solid was precipitated. The brown precipitate was extracted with boiling water (4 x 250 ml.) leaving a brown pitch and these extractions deposited the acid on standing overnight.

Yield = 4.5 g. acid + 5.3 g. pitch.

M.p. = 176-178°C.

Crystallisation from benzene/light petroleum gave white/

white elongated prisms, m.p. 185-6°C.

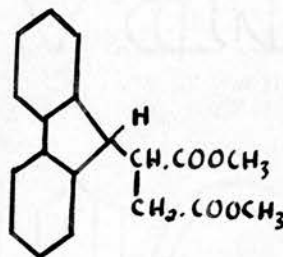
Analysis: Found C, 72.0%; H, 5.6%.

$C_{17}H_{14}O_4$ requires C, 72.33%; H, 5.0%.

Preparation of dimethyl-9-fluorenylsuccinate.

cf. C.A., 1944, 1248

or Alder and co-workers (Ber. 1942, 75B, 1511).



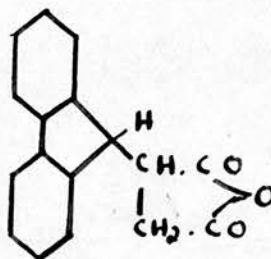
The acid (0.8 g.) was refluxed in methanol (10 ml.) containing concentrated sulphuric acid (0.5 ml.) for 45 minutes. The solution deposited the dimethyl ester on cooling. This crystallised from methanol in a felt of small needles.

Yield = 0.45 g. (52%)

M.p. = 115-116°C. (Lit. 120°C.)

Preparation of 9-fluorenylsuccinic anhydride.

The acid (1 g.) was refluxed for 3 hours with a mixture of acetic anhydride (10 ml.) and anhydrous zinc chloride in glacial acetic acid (10 ml. with 20 mg. zinc chloride per ml.). It was then poured into water (10 ml.) and the resulting precipitate extracted with ether. The ether layer was washed with potassium carbonate solution. The alkaline washings on acidification/



cation yielded no precipitation of an acid. The ether solution dried over anhydrous sodium sulphate was evaporated and left a white solid.

Crystallisation from ethyl acetate gave a white compound.

Yield = 0.75 g. (80%)

M.p. = 164-166°C. (Lit. 168°)

This experiment was an attempt at cyclisation of the acid but yielded only the anhydride.

Other attempted cyclisations.

1. A small quantity of the acid was dissolved in sulphuric acid (80% by weight) and this left for 24 hours. No product could be separated on treatment with water so it was concluded that sulphonation in the fluorene ring had taken place.

Experiments were also done varying the strength of the sulphuric acid, reaction time and temperature, but no cyclisation was obtained.

Sulphonation took place in most cases but in very mild conditions the original acid was regenerated.

2. The acid (1 g.) was added to syrupy phosphoric acid (5 ml.) and phosphorus pentoxide (5 g.) at 120° and the temperature raised to 150° over 5 minutes. After cooling and adding to water (30 ml.) the white solid/

solid precipitate was filtered.

Yield = 0.9 g.

M.p. = 163-165°C.

Mixed m.p. with 9-fluorenylsuccinic
anhydride (m.p. 164-166°) was 164-166°C.

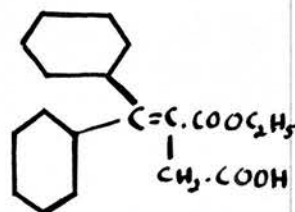
Stobbe Reaction on Benzophenone.

Method (1) which follows that of the original

Stobbe method (Ann., 282, 281; 308, 89).

Preparation of 3:3'-diphenyl-2-carbethoxyvinylacetic acid.

Benzophenone (10 g. 0.055 mol.)
was dissolved in diethyl succinate
(10 ml. 0.06 mol.) and ether (20 ml.
dried over sodium). This solution
was added drop by drop to a stirred
suspension of sodium methoxide (7.5 g. 0.14 mol.) in
dried ether (200 ml.) cooled in ice water. The
reaction mixture was set aside for 3 days in a
refrigerator, when the now brownish solution and
white precipitate were shaken up with two lots of
sodium hydroxide solution (each 50 ml. of 5%). The
ether solution was separated, washed with water, dried
over anhydrous sodium sulphate and evaporated. The
slightly discoloured oil obtained was refluxed for
one hour with sodium hydroxide solution when benzo-
phenone was separated.



Yield = 0.6 g.

The/

The sodium hydroxide extract was acidified with concentrated hydrochloric acid and an oily precipitate resulted.

Yield = 12.5 g.

The oil was extracted with light petroleum (b.p. 100-120°) from which an oil separated followed by white needles which on further crystallisation from light petroleum gave white needles.

Yield = 6.4 g.

M.p. = 117-118°C.

Quoted m.p. for 3:3'-diphenyl-2-carbethoxy-vinyl acetic acid is 124-125°C.

The residual oil obtained from the light petroleum (3.5 g.) was refluxed in sodium hydroxide solution (10%) for one and a half hours. The solution was treated with charcoal, and then acidified with concentrated hydrochloric acid, when a sticky whitish solid precipitated. On attempted crystallisation from aqueous alcohol a sticky solid was obtained at the foot of the test-tube and then white plates separated.

Yield = 1.3 g.

M.p. = 165-167°C.

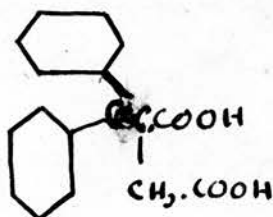
The sticky solid was extracted with water (2 x 25 ml.) and this allowed to cool. The resulting white precipitate was dissolved in excess alcohol, treated with charcoal, and hot water added to the filtered solution, till/

till precipitation almost took place. On cooling white plates separated.

Yield = 0.4 g.

M.p. = 168-169°C.

This was 3:3'-diphenyl-2-carboxyvinylacetic acid, m.p. 168-169°C. (Stobbe).



Method (2) cf. Johnson, Peterson and Schneider
(J.A.C.S., 1947, 69, 74)

The experimental procedure of the above workers was modified somewhat, and no nitrogen was used. Benzophenone (9-11 g., 0.05 mol.) was dissolved in diethyl succinate (13.05 g., 0.075 mol.) and this cooled solution added to a solution of potassium (2.15 g., 0.055 mol.) in tertiary-butyl alcohol (45 ml.). The resulting solution was refluxed for 30 minutes, when it was cooled and acidified with dilute hydrochloric acid. Water was added and the resulting oily precipitate taken up in ether. The ether layer was extracted several times with sodium hydroxide solution (2%) and these separated. On acidification with concentrated/

concentrated hydrochloric acid, the alkaline extracts gave a slightly sticky solid.

Yield = 9 g.

On crystallisation from a mixture of benzene and light petroleum white needles of 3:3'-diphenyl-2-carbethoxy-vinyl acetic acid were obtained.

Yield = 7.1 g.

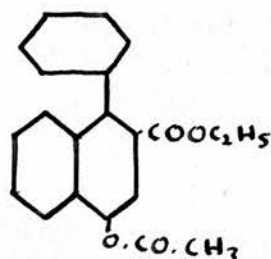
M.p. = 124-126°C. (Lit. 125-126°C)

Mixed m.p. with other Stobbe product (m.p. 117-118°C) is 121-124°C.

Cyclisation of 3:3'-diphenyl-2-carbethoxyvinylacetic acid to 1-phenyl-4-acetoxy-2-carbethoxy naphthalene.

cf. W. Borsche (Ann., 1936, 526, 9)

The ester acid (2 g.) was dissolved in acetic anhydride (5 ml.) and fused sodium acetate (0.55 g.) added. This mixture was refluxed for 30 minutes and then allowed to cool. The resulting brownish solid was shaken with water (50 ml.) and extracted with ether. The ether layer was washed with potassium carbonate solution (5%) and the washings on acidification with concentrated hydrochloric acid gave no precipitate. The ether solution, dried over anhydrous potassium carbonate, was evaporated to give a white solid.



Crystallisation/

Crystallisation from methanol gave white needles of the above naphthalene derivative.

Yield = 1.3 g.

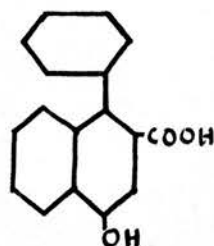
M.p. = 80-83°C. (Lit. 87-88°)

The mother liquor from the crystallisation was added to sodium hydroxide solution (20 ml. 10%) and the resulting suspension refluxed for one hour, when the solution had become clear. Acidification with dilute hydrochloric acid yielded a white solid, which crystallised from aqueous glacial acetic acid in white needles.

Yield = 0.17 g.

M.p. = 208-210°C. (Lit. 212-214°)

This was 1-phenyl-4-hydroxy-2-carboxynaphthalene.



Stobbe reaction on Fluorenone.

(1) Original method.

A solution of fluorenone (9 g., 0.05 mol.) in diethyl succinate (13 g., 0.075 mol.) and 100 ml. ether (dried over sodium) was gradually stirred into a suspension of sodium methoxide (7.5 g., 1.4 mol.) in dried ether (200 ml.) cooled in an ice-salt mixture. Stirring in the freezing mixture was continued for 3 hours and the reactants set aside for/

for 5 days in a refrigerator and then at ordinary temperatures for one day. An orange brown mass separated at the foot of the containing vessel, and this was filtered from the ether solutions and washed thoroughly with ether. The ether solution was washed with sodium hydroxide solution in which a slight brown precipitate settled, and then with water. After drying over anhydrous sodium sulphate the ether was evaporated to reveal a solution of fluorenone in diethyl succinate. The fluorenone was recovered by hydrolysis of the diethyl succinate to succinic acid soluble in sodium hydroxide.

Yield of fluorenone = 2.2 g.

The alkaline extract and washings and the precipitate insoluble in ether were added to boiling water (1.5 litres) in which they were completely soluble, but on acidification with concentrated hydrochloric acid, a brown dark mass was obtained which solidified on cooling.

Yield = 9.5 g.

The solution of this product in the minimum volume of boiling methyl alcohol deposited yellow needles.

Yield = 3.5 g.

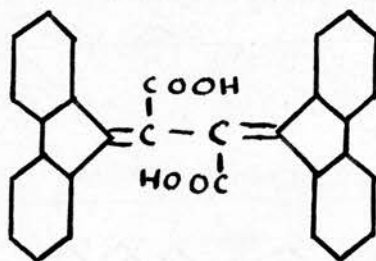
On heating this darkened above 130°C. to almost black at 170-180°C. to give a m.p. of 209-212°C. Further crystallisation/

crystallisation from methanol gave m.p. 212-213°C. with previous discoloration.

This compound was later proved to be 1:4-bis-diphenylene-2:3-dicarboxybutadiene.

Analysis: Found C, 81.14%; H, 4.30%.

$C_{30}H_{18}O_4$ requires C, 81.45%; H, 4.10%.



The methyl alcohol filtrate was evaporated down to leave a thick oil from which no crystalline product could be derived although it was soluble in alcohols, ether, acetone, benzene, etc., but insoluble in light petroleum.

Refluxing a portion of this product with sodium hydroxide for one hour gave on acidification unchanged material soluble in most of the usual organic solvents except light petroleum, and no crystalline compound was obtained.

Attempted esterification by refluxing with methanol containing concentrated sulphuric acid, produced a negligible amount of neutral oil and an acidic oil similar to the starting material.

The thick oil (2 g.) was refluxed with a mixture of/

of glacial acetic acid (100 ml.) and hydrobromic acid (100 ml.) and the solution poured into water. The brown flocculent precipitate began to melt about 90°C. and finally about 200°C. went liquid with decomposition. Attempts to crystallise this were unsuccessful, from all the usual organic solvents, though treatment with charcoal in alcohol was effective in cleaning up the colour of the product to an off-whitish yellow, no improvement was made in the melting-point or its non-crystalline form.

The experiment was also done using sodium ethoxide as the catalytic agent but similar results were obtained.

Attempts to esterify the 1:4-bisdiphenylene-2:3-di-carboxybutadiene by refluxing in ethanol or methanol containing sulphuric acid proved unsuccessful even after 24 hours refluxing.

However with diazomethane (cf. Organic Synthesis, XV, 4) a neutral compound was obtained, showing esterification had taken place.

The diazomethane was obtained in an ether solution by adding to a mixture of ether (100 ml.) and potassium hydroxide solution (30 ml. of 40%) nitrosomethylurea (10 g.) in small quantities with shaking/

shaking and cooling in ice water. The ether solution turned yellow and contained (theoretically at least) 2.8 g. diazomethane. The ether solution was decanted and dried over potassium hydroxide.

To a cooled solution of the acid (0.5 g.) in anhydrous ether (30 ml.) was added slowly the diazomethane solution (25 ml.). Evolution of nitrogen was evident and the reactants were set aside for 20 mins. after evolution of the gases had ceased. The excess diazomethane and the ether were evaporated in a water-bath in a very efficient fume cupboard to leave a pale yellow compound which crystallised from toluene in yellow octahedra, m.p. 224-225°C.

Yield = 0.32 g.

Analysis for 1:4-bisdiphenylene-2:3-dicarbomethoxy-butadiene:

Found C, 80.94%; H, 4.95%.

$C_{32}H_{22}O_4$ requires C, 81.66%; H, 4.79%.

*Bad
analysis.*

On refluxing this dimethyl ester (0.1 g.) in sodium hydroxide solution (50 ml.) for one hour it gradually went into solution and from the boiling orange solution an orange compound precipitated immediately on the addition of concentrated hydrochloric acid.

M.p. = 210-212°C. with discoloration to black about 180°C.

Mixed m.p. with the original acid (m.p. 204-212°C.) was 210-212°C.

Preparation/

Preparation of the di- γ -lactone from 1:4-bisdiphenylene-2:3-dicarboxybutadiene.

The diacid (5 g.) was refluxed in a solution of glacial acetic acid (600 ml.) and hydrobromic acid (400 ml. 34%) for 24 hours. The solution was poured into ice-water (2000 ml.) and the resulting white precipitate filtered.

Yield 4.7 g.

The product was dissolved in excess ethanol, the boiling solution treated with charcoal, filtered, and boiling water added to the colourless hot solution until near precipitation point. On cooling white prisms were deposited.

M.p. = 284-286°C. with a yellow coloration appearing above 240°C.

Analysis: Found C, 81.53%; H, 4.27%.

$C_{30}H_{18}O_4$ requires C, 81.45%; H, 4.10%.

Properties of the above compound.

It was insoluble in cold sodium hydroxide solution but on refluxing (1 g.) with sodium hydroxide solution for 2 hours it was gradually entirely converted to a yellow compound which completely dissolved in the boiling diluted solution. On acidification with concentrated hydrochloric acid the boiling solution immediately deposited a yellow precipitate.

Yield = approximately 1 g.

m.p./

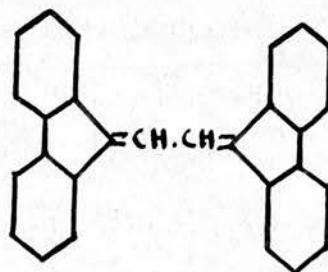
M.p. = 206-210°C. with previous discoloration.
Crystallisation from methanol yielded yellow needles,
m.p. 212-213°C. with previous discoloration.
Mixed m.p. with 1:4-bisdiphenylene-2:3-dicarboxy-
butadiene (m.p. 212-213°C.) is 212-213°C.

Attempts to form the anhydride of the anhydride
of the 1:4-bisdiphenylene-2:3-dicarboxybutadiene were
unsuccessful. In all cases quoted below a deep
purple semi-solid was formed which defied all attempts
at crystallisation from all the normal organic solvents
in all of which the compound was soluble excepting
light petroleum.

- (1) Treating the solid with acetyl chloride in the
cold and evaporation of the acetyl chloride on a
steam bath to leave the deep purple semi-solid.
- (2) Refluxing with acetyl chloride and subsequent
evaporation to a similar product.
- (3) Refluxing with acetic anhydride and glacial acetic
acid (50:50 mixture) with a catalytic amount of
anhydrous zinc chloride present. Similar product
was obtained after adding to water.

Preparation of 1:4-bisdiphenylenebutadiene or 1:2-di-
fluorenelidene ethane.

The 1:4-bisdiphenylene-
2:3-dicarboxybutadiene (0.5 g.)
was dissolved in warm quinoline
(20 ml.) and copper bronze
added. The mixture was heated
in an oil bath when bubbles of
carbon/



carbon dioxide began to appear at 160°C. and this gaseous evolution became fairly vigorous at 180°C., at which temperature the oil bath was kept for 20 mins. after evolution of gases had ceased. The hot quino- line solution was poured into dilute hydrochloric acid (100 ml.) and the resulting brown precipitate filtered. This was washed with acetone to remove all soluble impurities, leaving a deep red compound, which dissolved in boiling xylene. The solution was filtered from copper bronze, the filtrate depositing orange red needles of the required compound.

Yield = 0.3 g.

M.p. = 368-370°C. with sublimation just before the m.p.

The melting-point was done in a fused sodium nitrate, potassium nitrate mixture and was uncorrected, but agrees with that obtained by Wislicenus (Ber., 1915, 48, 619) m.p. 372-374°C.

Analysis: Found C, 93.5%; H, 5.20%.

Calculated for $C_{28}H_{18}$: C, 94.81%; H, 5.16%.

As quoted by Wislicenus this compound gave in a nitrobenzene solution with anhydrous aluminium chloride, a red colour, turning to a dark green, and with fuming sulphuric acid in the cold gave a blue colour, turning green.

*Bad
Analysis*

A suspension of this compound (0.2 g.) in glacial acetic acid (30 ml.) was refluxed for one hour with zinc dust (5 g.) when all red particles had disappeared. The filtered solution deposited colourless needles, m.p. 258-260°C.

Yield = 0.12 g.

Recrystallised from glacial acetic acid m.p. 262-264°C., compound turning yellow above 240°C.

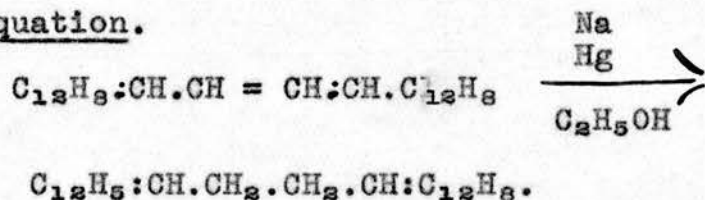
According to Wislicenus (Ber., 1915, 48, 622) this compound is 1:4-bisdiphenylenebutylene (m.p. 267-268°C.)

According also to Wislicenus (loc. cit.) the reduction can be taken a stage further to 1:4-bisdiphenylenebutane (m.p. 224-225°C.).

The 1:4-bisdiphenylenebutylene was refluxed with sodium amalgam in aqueous alcohol (30 ml.) for 2 hours. The syrupy solution was decanted and filtered and on cooling slowly deposited white prisms, m.p. 222-224°C. Crystallised from benzene/light petroleum, m.p. 224-225°C.

Thus was Wislicenus's work confirmed.

Equation.



Results of Ebulliscope Molecular Weight Determinations.

in ethyl acetate following the method of Menzies and Wright (J.A.C.S., 1921, 43, 2310).

Product from Stobbe condensation (Method 1)

i.e. 1:4-bisdiphenylene-2:3-dicarboxybutadiene.

Found for M.W. a) 420
 b) 456

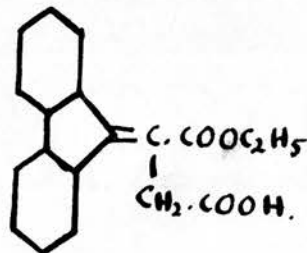
Theoretical M.W. is 442.

Stobbe Reaction on Fluorenone.

(2) Modified Method.

Preparation of 3:3'-diphenylene-2-carbethoxyvinyl-acetic acid.

Fluorenone (9 g., 0.05 mol.) was dissolved in diethyl succinate (13.08 g., 0.075 mol.) and tertiary-butyl alcohol (30 ml.). This solution



was cooled to 0°C., when a little fluorenone separated out, and then added to a frozen (at 0°C.) solution of potassium (2.15 g., 0.055 mol.) in tertiary-butyl alcohol (45 ml.). The reaction mixture was heated gently, and finally gently refluxed until it had been heated for 35 minutes. (As soon as heat was applied the mixture turned a very dark brown). The solution was cooled and acidified with dilute hydrochloric acid. After dilution to 600 ml. the orange oil which separated was extracted with ether, and the ether layer washed/

washed several times with water, before being extracted with sodium hydroxide solution (5%). The ether layer, dried over anhydrous sodium sulphate was evaporated down to an orange oil which was a solution of fluorenone in diethyl succinate. The fluorenone was separated by hydrolysis of the diethyl succinate with sodium hydroxide solution (20%) and filtering off the solid remaining undissolved in the cooled solution.

Yield = 1.7 g.

Crystallised from benzene/light petroleum gave yellow needles, m.p. 80-82°C.

Mixed m.p. with fluorenone (m.p. 82-84°C.) is 81-83°C.

The sodium hydroxide extract yielded an orange oil, which was extracted with ether. The ether solution was washed with water, and after drying over anhydrous sodium sulphate was evaporated to give an orange oil.

Yield = 11.7 g.

The oil was dissolved in carbon disulphide (20 ml.) and left overnight when a whitish compound crystallised out. This was filtered and washed with a small quantity of carbon disulphide, m.p. = 95-102°C.

Crystallisation from benzene gave m.p. 120-123°C.

Yield = 3.5 g.

On heating the benzene solution and adding light petroleum a further yield of compound was obtained, m.p. 121-124°C.

Total/

Total yield = 4.4 g. (29.5%)

A sample crystallised from benzene several times gave very pale yellow needles of the 3:3'-diphenylene-2-carbethoxyvinylacetic acid, m.p. 126-127°C.

Analysis: Found C, 73.6%; H, 5.33%.

$C_{19}H_{16}O_4$ requires C, 74.01%; H, 5.23%.

The carbon disulphide solution was then allowed to evaporate and the brown oily residue was dissolved in the minimum of hot methanol. On cooling yellow needles separated, which went orange on exposure to light.

Yield = 0.6 g. (5.4%)

M.p. = 208-210°C. with previous darkening in colour.

Mixed m.p. of this compound with 1:4-bisdiphenylene-2:3-dicarboxybutadiene (m.p. 212-213°C.) was 209-211°C. with previous discoloration to almost black. The alcoholic solution was added to sodium hydroxide solution (75 ml., 10%) and refluxed for one and a half hours. After dilution to 150 ml. the solution was boiled and treated with charcoal, filtered, and the clear brown filtrate acidified to give a yellow brown precipitate.

Yield = 3.3 g. (24.4%)

M.p. = 200-204°C. (with softening and discoloration above 196°C.)

Mixed/

Mixed m.p. with 3:3'-diphenylene-2-carboxyvinylacetic acid (p.104³) of m.p. 204-206°C. was 202-204°C. with softening above 200°C.

Total yield of mono-condensation product = 53.9%.

Total yield of di-condensation product = 5.4%.

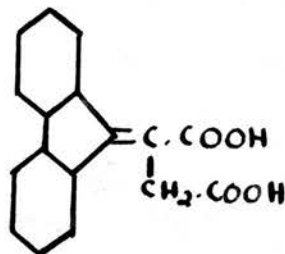
Total yield of recovered fluorenone = 18.9%.

This experiment, repeated, using double quantities of the initial reagents and heating for the same length of time produced equivalent yields of the three products listed above.

Hydrolysis of 3:3'-diphenylene-2-carbethoxyvinyl-acetic acid to 3:3'-diphenylene-2-carboxyvinyl-acetic acid.

The ester acid (1 g.) was refluxed in a sodium hydroxide solution for 1 hour. After cooling and diluting to 60 ml.

the solution was filtered and then acidified with concentrated hydrochloric acid when yellow needles were precipitated.



Yield = 0.95 g.

M.p. = 201-204°C.

Yellow-orange needles were obtained from comparatively large volumes of benzene, m.p. 205-206°C. with discoloration and softening from 200°C.

Analysis/

Analysis: Found: C, 72.86%; H, 4.32%.

$C_{17}H_{12}O_4$ requires C, 73.5%; H, 4.3%.

Esterification of 3:3'-diphenylene-2-carbethoxyvinyl-acetic acid.

This proved to be rather troublesome.

(1) The diacid (0.4 g.) was refluxed with ethanol (5 ml.) containing concentrated sulphuric acid (4 drops) for 4 hours, and was then added to water. The oily precipitate was extracted with ether, and the ether solution, washed with potassium carbonate solution. Acidification of the washings produced a yellow solid.

Yield = 0.25 g.

M.p. = 199-202°C.

Mixed m.p. with starting material (201-204°C.) was 201-204°C.

The ether layer was dried over anhydrous sodium sulphate, and the ether evaporated. The brownish oily residue was dissolved in the minimum of hot methanol, and on cooling deposited rosettes of yellow needles.

Yield = 0.07 g.

M.p. = 79/81°C.

Mixed m.p. with ethyl 3:3'-diphenylene-2-carbethoxyvinyl acetate (p.109) of m.p. 84°C. is 81-83°C.

79-81°C.

(2) /

(2) The dibasic acid (0.5 g.) was refluxed for 24 hours in ethanol (10 ml.) containing concentrated sulphuric acid (1 ml.), added to water and the resulting oily precipitate taken up in ether. The ether layer was washed several times with water and then with potassium carbonate solution. The ether layer, dried over anhydrous potassium carbonate was evaporated and yielded a yellowish brown oil which became solid on trituration with a little methanol. It crystallised in rosettes of needles from methanol.

Yield = 0.12 g.

M.p. = 78-80°C.

Mixed m.p. with ethyl 3:3'-diphenylene-2-carbethoxy-vinyl acetate (p.109) of m.p. 83-84°C. was 80-82°C.

The alkaline extract was acidified with concentrated hydrochloric acid, and an orangish precipitate formed.

Yield = 0.28 g.

This crystallised in rosettes of fine needles from benzene, m.p. 127-128°C.

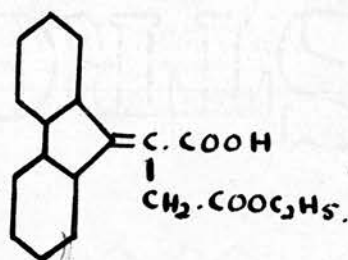
If heating of the compound was continued above m.p. the melt became solid at about 170° and finally melted at 202-204°C.

Mixed m.p. of this new solid with the anhydride of the dibasic acid (p.110) of m.p. 211-212°C. was 206-208°C.

Mixed/

Mixed mp. of acid product with 3:3'-diphenylene-2-carbethoxyvinyl acetic acid (m.p. 126-127°C.) was 105-110°C.

Therefore new compound (m.p. 127-128°C.) was taken to be ethyl 3:3'-diphenylene-2-carboxyvinyl acetate.



Analysis: Found: C, 73.68%; H, 5.15%.

$\text{C}_{19}\text{H}_{16}\text{O}_4$ requires C, 74.01%; H, 5.21%.

(3) The above experiment (2) was repeated using methanol with the dibasic acid (0.45 g.)

The ether layer contained a slight amount of oil from which no solid could be separated, and the carbonate extracts yielded on acidification an orange compound.

Yield = 0.36 g.

This crystallised from benzene in pale yellow rosettes of needles, m.p. 125-126°C., but the melt when solid again at 140°C. and finally melted at 203-205°C. as was the case with compound obtained in (2).

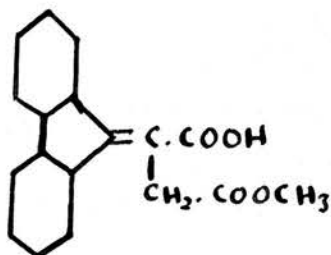
The mixed m.p. of this compound (m.p. 125-126°C.) was/

was 112-117°C. showing that these were different compounds, though the melt again solidified about 150°C. and finally melted at 202-204°C., showing that both change to the same compound, namely the anhydride of the dibasic acid.

It was concluded that the compound formed in this experiment was the methyl 3:3'-diphenylene-2-carboxyvinyl acetate.

Analysis: Found: C, 71.6%; H, 4.19%.

$C_{18}H_{14}O_4$ requires C, 73.49%; H, 4.79%.



Preparation of the methyl and ethyl esters of 3:3'-diphenylene-2-carbethoxyvinylacetic acid.

The ester acid (0.5 g.) was dissolved in the alcohol (5 ml.) containing concentrated sulphuric acid (4 drops) and the solution refluxed for 45 mins. After cooling and adding to water (50 ml.) the oily precipitate was extracted with ether. The ether layer after separation was washed with water, and sodium hydroxide solution and again with water. After drying over anhydrous sodium sulphate and evaporation, the/

the ether layer gave pale yellow solids, which were crystallised from methanol.

(1) Methanol gave yellow needles of

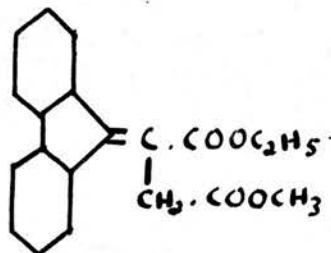
methyl 3:3'-diphenylene-2-carbethoxyvinyl acetate.

Yield = 0.39 g. (74%)

M.p. = 93-94°C.

Analysis: Found: C, 73.51%; H, 5.44%

$C_{20}H_{18}O_4$ requires C, 74.52%; H, 5.63%.



(2) Ethanol gave yellow needles of

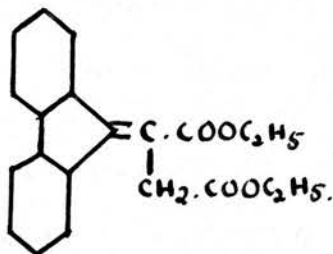
ethyl 3:3'-diphenylene-2-carbethoxyvinyl acetate.

Yield = 0.41 g. (73%)

M.p. = 83-84°C.

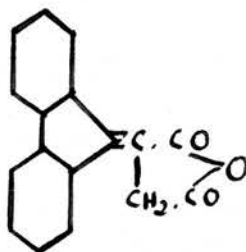
Analysis: Found: C, 73.75%; H, 5.93%.

$C_{21}H_{20}O_4$ requires C, 74.97%; H, 5.99%



Preparation of the anhydride of 3:3'-diphenylene-2-carboxyvinylacetic acid.

(1) From 3:3'-diphenylene-2-carboxyvinylacetic acid.



The ester acid (0.7 g.)

was dissolved in a mixture of acetic anhydride (5 ml.) and glacial acetic acid, containing zinc chloride (5 ml. of 20 mg. per ml.) and after refluxing for 4 hours the mixture was allowed to cool when long needles were obtained.

Yield = 0.45 g.

M.p. = 200-204°C.

Crystallisation from glacial acetic acid gave needles m.p. 203-205°C. (with no discoloration previous to melting).

Mixed m.p. with 3:3'-diphenylene-2-carboxyvinylacetic acid (m.p. 205-206°C. with discoloration and softening from 200°C. onwards) is 203-206°C. with discoloration. This experiment was an attempted cyclisation.

Analysis: Found: C, 76.63%; H, 3.78%.

$C_{17}H_{10}O_3$ requires C, 77.83%; H, 3.83%.

(2) From 3:3'-diphenylene-2-carboxyvinylacetic acid.

The diacid (1 g.) was dissolved in acetyl chloride (40 ml.) and set aside for 2 hours, when much of the acetyl chloride had evaporated, and a yellow/

yellow feathery precipitate had formed. Dried (over sodium) benzene (25 ml.) was added to dissolve the precipitate and the resulting mixture warmed gently to evaporate the excess acetyl chloride. The hot benzene solution was evaporated to 10 ml. and from it crystallised clear yellow elongated prisms.

Yield = 0.72 g.

M.p. = 211-212°C. (no discoloration before melting)

Mixed m.p. with compound obtained in (1) was 208-210°C.

Mixed m.p. with the original dibasic acid (m.p. 205-206°C. with previous softening and discoloration above 200°C.) was 208-211°C. (with discoloration from 200°C. onwards).

Analysis: Found: C, 77.01%; H, 3.84%.

$C_{17}H_{10}O_3$ requires C, 77.83%; H, 3.83%.

Reduction of 3:3'-diphenylene-2-carboxyvinylacetic acid to 9-fluorenylsuccinic acid.

The diacid (0.4 g.) was dissolved in glacial acetic acid (10 ml.) and zinc dust (2 g.) added to the refluxing solution. Refluxing was continued for 20 minutes, when the originally yellow solutions had been colourless for 10 minutes. The mixture was poured into water (90 ml.) and extracted with ether. The ether solution was extracted with potassium carbonate/

carbonate solution (5%) and this separated. The ether solution then contained nothing. On acidification the potassium carbonate extract gave a white solid.

Yield = 0.37 g.

M.p. = 181-184°C.

Mixed m.p. with 9-fluorenylsuccinic acid (m.p. 185-186°C.) was 182-185°C.

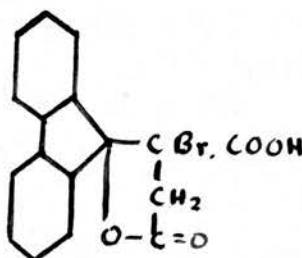
The product obtained above (0.1 g.) was refluxed in methanol (3 ml.) containing sulphuric acid (2 drops) for 30 min. The solution was diluted to 7 ml. with hot water and a feathery crystalline compound was obtained on cooling.

M.p. = 108-111°C.

Mixed m.p. with dimethyl 9-fluorenylsuccinate (m.p. 115-116°C.) was 112-115°C.

Preparation of 3:3'-diphenylene-2-carboxy-2'-bromobutyro-γ-lactone.

(1) 3:3'-diphenylene-2-carboxyvinylacetic acid (1 g.) was dissolved in hot glacial acetic acid (3 ml.) and to this was added bromine (0.6



ml.). Heating was continued for a short time and the tube set aside when a crystalline solid separated out/

out. Crystallisation from chlorobenzene gave white prisms.

Yield = 0.2 g.

M.p. = 218-219°C.

The filtrate was added to water and the resulting brown oil taken up in ether. The ether layer was washed with water, dried over anhydrous sodium sulphate, and evaporated. The resulting brown oil was triturated with benzene to give a white solid which crystallised in prisms from chlorobenzene.

Yield = 0.3 g.

M.p. = 220-222°C.

Mixed m.p. with other solid obtained (m.p. 218-219°C.) was 219-221°C.

Analysis: Found: Br, 24.32%.

$C_{17}H_{11}O_4Br$ requires Br, 22.78%.

(2) To a cold solution of ethyl 3:3'-diphenylene-2-carboxyvinylacetate (0.2 g.) in acetic acid (2 ml.) was added excess bromine (0.2 ml.) and the solution left for 3 hours, when it had appreciably lightened in colour. Water was added, and the resulting oily precipitate taken up in ether. The ether layer was washed with water, then with sodium bisulphite to destroy excess bromine, and was finally dried over anhydrous sodium sulphate, before being evaporated to yield/

yield a brown oil which on trituration with benzene yielded a white solid. On heating with benzene (3 ml.) a portion of the solid remained undissolved and the benzene solution was filtered.

Yield = 0.075 g.

M.p. = 224-225°C.

Mixed m.p. with 3:3'-diphenylene-2-carboxy-2'-bromobutyro- γ -lactone (m.p. 218-219°C.) was 222-224°C.

A small quantity of white solid separated from the benzene extract, m.p. = 222-224°C.

Mixed m.p. with the above product = 224-225°C.

This experiment was repeated with the methyl-3:3'-diphenylene-2-carboxyvinylacetate when the same compound was obtained in similar yield.

A small quantity of the 3:3'-diphenylene-2-carboxy-2-bromobutyro- γ -lactone was refluxed with sodium hydroxide (5 ml. of 10%) for 20 minutes and the clear solution acidified with concentrated hydrochloric acid, when white needles were slowly deposited from the now turbid solution.

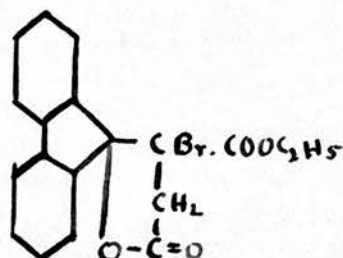
M.p. = 228-230°C.

Mixed m.p. with 3:3'-diphenylene-2-carboxybutylenolactone (p.117) of m.p. 230-231°C. was 229-231°C.

Preparation/

Preparation of 3:3'-diphenylene-2-carbethoxy-2'-bromo-
butyro- γ -lactone.

- (1) From 3:3'-diphenylene-2-
carbethoxyvinylacetic
acid.



The ester acid (1 g.) was dissolved in cold glacial acetic acid (3 ml.) and bromine (0.6 g.) added. This was set aside and the originally orange solution gradually lost colour, and when almost colourless, a white crystalline precipitate appeared. After another 30 minutes this was filtered.

Yield = 0.65 g.

M.p. = 145-148°C.

This crystallised from benzene-light petroleum (b.p. 60-80°) in fine white needles, m.p. 149-150°C.

The filtrate was diluted with a large volume of water and the precipitate formed, was taken up in ether. The ether solution was washed with potassium carbonate solution, water, dried over anhydrous sodium sulphate, and evaporated to give a white sticky solid which crystallised from benzene/light petroleum (b.p. 60-80°) mixture in white needles.

Yield = 0.26 g.

M.p. = 147-148°C.

Mixed/

Mixed m.p. with above product = 148-150°C.

The alkaline washings on acidification only produced a very slight turbidity.

Analysis: Found: Br, 20.52%.

$C_{19}H_{15}O_4Br$ requires Br, 20.64%.

(2) From ethyl 3:3'-diphenylene-2-carbethoxyvinyl acetate.

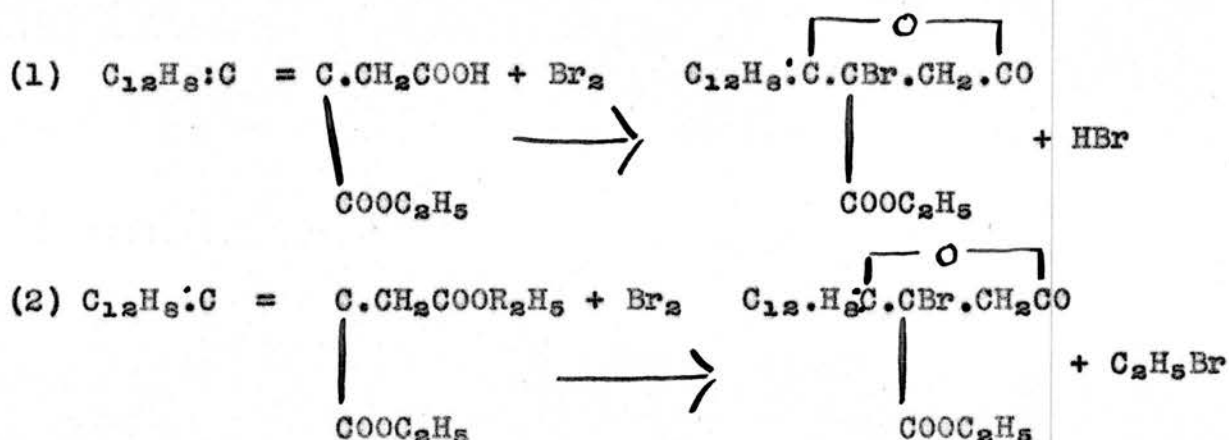
The diester (0.2 g.) was dissolved in glacial acetic acid (2 ml.) and bromine (0.12 g.) added, and the solution set aside for 2 hours, when the originally brown solution became practically colourless. It was then added to water (30 ml.) and the resulting white suspension extracted with ether. The ether layer was washed with potassium carbonate solution, then with water, and dried over anhydrous sodium sulphate. Evaporation of the ether left a white solid which crystallised from benzene/light petroleum in white needles.

Yield = 0.15 g.

M.p. = 147-149.

Mixed m.p. with 3:3'-diphenylene-2-carbethoxy-2'-bromobutyro- γ -lactone (m.p. 149-150°C.) is 148-150°C. Equations for the reaction are:

(1) /



3:3'-diphenylene-2-carboxybutyleno-γ-lactone.

and its reduction to 9-fluorenylsuccinic acid.

Preparation.

(1) 3:3'-diphenylene-2-carbethoxy-2'-bromobutyro-γ-lactone

(0.5 g.) was refluxed for 40

mins. with a mixture of glacial

acetic acid (5 ml.) and hydrobromic acid (5 ml., 34%)

and then poured into water (40 ml.). The precipitate

was taken up in ether, and the ether layer washed

several times with water, before being extracted with

potassium carbonate solution. The ether layer was

dried over anhydrous potassium carbonate solution and

then evaporated to yield a negligible quantity of oil.

On acidification with concentrated hydrochloric acid,

the carbonate extracts slowly deposited white needles.

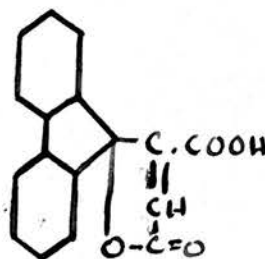
Yield = 0.4 g.

M.p. = 220-224°C.

These crystallised from chlorobenzene in prisms, m.p.

228-229°C.

(2)/



(2) The bromo-lactone-ester (0.2 g.) was also refluxed with sodium hydroxide solution (10%, 5 ml.) for 30 mins., and the cooled clear solution acidified with concentrated hydrochloric acid when again white needles were slowly deposited.

Yield = 0.17 g.

M.p. = 226-228°C.

These crystallised from chlorobenzene in prisms, m.p. 230-231°C.

Mixed m.p. with product from method (1) is 229-230°C.

Analysis: Found: C, 71.58%; H, 3.75%.

$C_{17}H_{10}O_4$ requires C, 73.4%; H, 3.6%.

Reduction

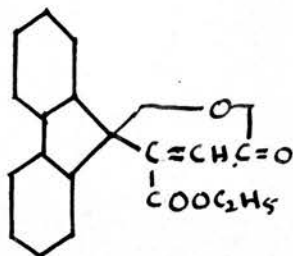
The unsaturated lactone (0.1 g.) was refluxed in glacial acetic acid (5 ml.) with zinc dust (1 g.), the solution decanted into water and the resulting precipitate taken up in ether. The ether layer was washed with water and then extracted with potassium carbonate solution. After drying over anhydrous potassium carbonate, the ether solution was evaporated to yield a negligible quantity of brown oil. The carbonate extract on acidification with concentrated hydrochloric acid gave immediately a white precipitate.

Yield = 0.07 g.

M.p. = 182-184°C.

Mixed m.p. with 9-fluorenylsuccinic acid (m.p. 185-186°C.) was 184-186°C.

Preparation of 3:3'-diphenylene-2-carbethoxybutyleno- γ -lactone.



3:3'-diphenylene-2-carbethoxy-2'-bromobutyro- γ -lactone (0.5 g.) was dissolved in dry pyridine (5 ml.) and the solution kept just below boiling point for 1 hour when it had become brown in colour. On addition to water (25 ml.) a discoloured white solid was precipitated. It crystallised from methanol in fine white needles.

Yield = 0.28 g.

M.p. = 124-125°C.

Analysis: Found: C, 73.55%; H, 4.62%.

$C_{19}H_{14}O_4$ requires C, 74.5%; H, 4.60%.

Bad analysis

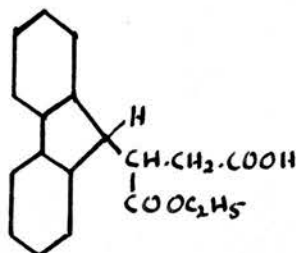
This compound (0.2 g.) was refluxed for 30 mins. with sodium hydroxide solution (10 ml. of 10%) in which it gradually dissolved, solution being complete within 10 mins. On acidification of the hot solution with concentrated hydrochloric acid white needles were slowly deposited.

Yield = 0.16 g.

M.p. = 227-229°C.

Mixed m.p. with 3:3'-diphenylene-2-carboxybutyleno- γ -lactone (p.117) of m.p. 230-231°C. was 228-230°C.

Preparation of 3:3'-diphenylene-2-carbethoxybutyric acid (9-fluorenylsuccinic acid-b-monoethyl ester)



3:3'-diphenylene-2-carbethoxyvinylacetic acid (1 g.) was dissolved in glacial acetic acid (20 ml.) and zinc dust (3 g.) added. This mixture was refluxed for 1 hour, during which time the pale yellow solution became absolutely colourless. It was then poured into water (60 ml.) and the white precipitate extracted with ether. The ether solution was washed with water, extracted with potassium carbonate solution, washed again with water, and finally evaporated to yield a negligible quantity of oil after drying over anhydrous sodium sulphate. The carbonate extract on acidification with concentrated hydrochloric acid gave a white solid.

Yield = 0.91 g.

M.p. = 164-166°C.

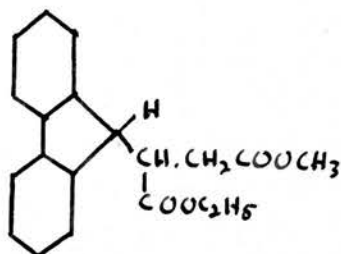
Crystallisation from benzene gave a felt of small needles, m.p. 168-169°C.

Analysis: Found: C, 73.4%; H, 6.02%.

$C_{19}H_{18}O_4$ requires C, 73.53%; H, 5.85%.

Preparation/

Preparation of methyl:3:3'-diphenylene-2-carbethoxy-
butyrate.



Methyl 3:3'-diphenylene-2-carbethoxyvinyl acetate (0.2 g.) was treated with zinc and glacial acetic acid as in the above experiment, but in this case, nothing was obtained on acidification of the carbonate extract but the neutral product was obtained from the dried ether solution and crystallised from methanol in a felt of needles.

Yield = 0.14 g.

M.p. = 93-94°C.

Mixed m.p. with starting material (m.p. 93-94°C.) was 70-78°C.

Analysis: Found: C, 73.4%; H, 6.25%.

$C_{20}H_{20}O_4$ requires C, 74.06%; H, 6.22%.

Hydrolysis of 3:3'-diphenylene-2-carbethoxybutyric acid
to 9-fluorenylsuccinic acid.

The ester-acid (0.2 g.) was refluxed in a sodium hydroxide solution (10 ml.) for 30 mins. and the cooled solution acidified with concentrated hydrochloric/

hydrochloric acid to yield a white precipitate.

Yield = 0.17 g.

M.p. = 182-185°C.

Mixed m.p. with 9-fluorenylsuccinic acid (m.p. 185-186°C.) was 183-185°C.

Action of zinc dust and glacial acetic acid on 3:3'-diphenylene-2-carbethoxy-2'-bromobutyro-γ-lactone.

The compound (0.5 g.) was refluxed with glacial acetic acid (10 ml.) and zinc dust (2 g.) for 1 hour and the mixture then added to water (50 ml.). The white precipitate was extracted with ether, the ether layer washed with water, and then with potassium carbonate solution (5%), dried over anhydrous potassium carbonate, and evaporated to yield a negligible amount of oil. The carbonate extract was acidified with concentrated hydrochloric acid when a white precipitate appeared.

Yield = 0.37 g.

M.p. = 159-163°C.

Crystallisation from benzene/light petroleum gave a felt of white needles, m.p. 164-165°C.

Mixed m.p. with 3:3'-diphenylene-2-carbethoxybutyric acid (m.p. 168-169°C.) was 167-169°C.

Properties/

Properties of 3:3'-diphenylene-2-carbethoxybutyric acid.

(1) Hydrolysis. The compound (0.15 g.) was refluxed with sodium hydroxide solution (10 ml.) for 30 mins. and the solution acidified with concentrated hydrochloric acid when a white precipitate was obtained.

Yield = 0.14 g.

M.p. = 183-184°C.

Mixed m.p. with 9-fluorenylsuccinic acid (m.p. 185-186°C.) was 184-186°C.

(2) Formation of the methyl ester.

The compound (0.2 g.) was refluxed in methanol (2 ml.) containing concentrated sulphuric acid (1 drop) for 30 mins. and poured into water. The white precipitate was extracted with ether and the ether solution washed with potassium carbonate solution. The carbonate washings yielded no precipitate on acidification. The ether layer after drying over anhydrous sodium sulphate was evaporated to a slightly discoloured oil which soon goes solid. Crystallisation from methanol gave a felt of white needles.

Yield = 0.11 g.

M.p. = 88-90°C.

Mixed m.p. with methyl 3:3'-diphenylene-2-carbethoxybutyrate (m.p. 93-94°C.) was 91-93°C.

Decarbethoxylation/

Decarboxylation of 3:3'-diphenylene-2-carbethoxy-vinylacetic acid to 3:3'-diphenylenebutyro- γ -lactone.

The ester-acid (1 g.) was refluxed in a mixture of glacial acetic acid (20 ml.) and hydrobromic acid (20 ml. of 34%) for 4 hours. The brown solution was allowed to cool slowly and a felt of needles gradually separated out. On filtration a yellowish crystalline solid was obtained.

Yield = 0.8 g.

Crystallisation from benzene gave a felt of white needles, m.p. 197-199°C. These very white needles gave a blue fluorescence in ultra-violet light, a characteristic of pure 3:3'-diphenylenebutyro- γ -lactone.

Mixed m.p. of the product with 3:3'-diphenylenebutyro- γ -lactone (p. 66) (m.p. 200-201°C.) was 199-200°C.

Note: Decarboxylation of the diacid, 3:3'-diphenylene-2-carboxyvinylacetic acid, to the same product can be effected in the same way.

The product obtained above (0.5 g.) was refluxed for 45 mins. with red phosphorus (0.4 g.) and hydriodic acid (5 ml., d = 1.9) and the procedure followed as for the preparation of 9-fluorenyl-2-propionic acid (p. 65). A white solid was obtained.

Yield /

Yield = 0.47 g.

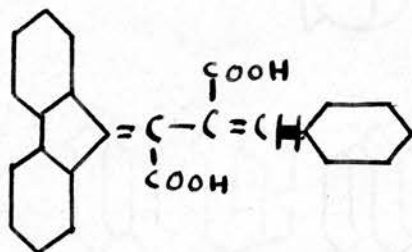
M.p. = 139-142°C.

Mixed m.p. with 9-fluorenyl-2-propionic acid (m.p. 143-144°C.) was 141-142°C.

Therefore 9-fluorenyl-2-propionic acid had been obtained.

← 2/16/48

Preparation of 1-(9-fluorenylidene)-2-benzylidene-succinic acid or 1-diphenylene-4-phenyl-2-3-dicarboxybutadiene.



Ethyl 3:3'-diphenylene-2-carbethoxybutyric ^{ate} acid (1.7 ^g m., 0.005 mol.) and benzaldehyde (1 ml., 0.01 mol.) were dissolved in dried (over sodium) ether (20 ml.) and sodium methoxide (0.6 g., 0.11 mol.) added. The mixture was left in a refrigerator for 5 days when the resulting brown precipitate filtered from the brown ether solution and washed thoroughly with ether before being completely dissolved in water. The ether filtrate and washings were extracted with sodium hydroxide solution, and these alkaline extractions/

and/

extractions added to the aqueous solution. The separated ether layer was washed with water, dried over anhydrous sodium sulphate, and evaporated to yield a little benzaldehyde. The alkaline aqueous solution was now acidified with concentrated hydrochloric acid, and ^avery sticky solid was precipitated, which was extracted with ether. The ether solution after washing with water, was dried over anhydrous sodium sulphate and evaporated to give a brown oil which on heating with benzene and cooling produced an orange solid.

Yield = 0.85 g.

M.p. = 195-198°C.

On heating with a little chlorobenzene a portion of the compound dissolved and the orange residue was filtered, m.p. 204-206°C. with darkening in colour above 150°C.

On cooling the chlorobenzene deposited a solid, m.p. 201-204°C.

Mixed m.p. with insoluble compound above (m.p. 204-206°C.) was 202-206°C.

Mixed m.p. with 3:3'-diphenylene-2-carboxyvinylacetic acid (m.p. 205-206°C.) was 185-190°C.

Mixed m.p. with 1-(9-fluorenylidene)-2-benzylidene succinic acid (prepared by method given by Stobbe, Ann. 1911, 380,126) of m.p. 202-206°C. (Lit. 206-208°C.) was 203-206°C.

C₆₈₂.

Attempted cyclisations on 3:3'-diphenylene-2-carbethoxyvinyl acetic acid.

(1) The ester acid (2 g.) was treated with thionyl chloride to convert it to the acid chloride, and the excess thionyl chloride removed under reduced pressure at 50°C. Light petroleum (b.p. 100-120°) was added and this removed under the same conditions. Light petroleum (20 ml.) (b.p. 100-120°) was then added and anhydrous aluminium chloride (1 g.) dropped into the solution while it was refluxed on a steam bath. Refluxing was continued for one hour, when the solution was cooled and the contents of the flask alternately extracted with ether and sodium hydroxide solution. The ether layer was washed with water, dried over anhydrous sodium sulphate and evaporated to yield a negligible quantity of a purple oil. The alkaline extracts were filtered to a clear solution and were acidified to give brown semi-solid mass from which no crystalline compound could be obtained.

(2) The ester acid (2 g.) was refluxed for 30 mins. with acetic anhydride (5 ml.) and sodium acetate (0.55 g.) and then allowed to cool, when it was shaken up with water. A purple oil was obtained which was extracted with ether. The ether solution was washed with potassium carbonate solution, but these washings on/

on acidification produced no compound. The ether layer was dried over anhydrous sodium sulphate and evaporated to give a purple oil which was dissolved in benzene (5 ml.) and chromatographed on a column of alumina (6" x $\frac{3}{8}$ ").

The main bulk of the material was washed through the column immediately with no separation even though a mixture of benzene (2 parts) and light petroleum (1 part) was used.

From the first 30 ml. of washings collected corresponding to a deep red band, a deep red oil was obtained which on trituration with methanol gave a dark purple solid, m.p. 100-140°C. Yield = 1.5 g.

Attempts were made to crystallise this solid from most of the usual organic solvents but no improvement in the melting-point was recorded.

This solid (0.4 g.) was dissolved in benzene (10 ml.) and was again chromatographed over alumina (6" x $\frac{3}{8}$ "), washing through the column being effected by benzene (1 part), light petroleum (1 part). No separation occurred so the column was extracted with alcohol when the original compound was obtained in the same impure state.

Yield = 0.31 g.

On further washing of the original column with benzene, then with ether, and finally with alcohol, only/

only small quantities of brown oils (total yield about 0.1 g.) were obtained.

This experiment was repeated, with a shorter reaction time (10 mins.) and with a longer reaction time (1 hour), when in both cases essentially similar results were recorded.

(3) The ester acid (1 g.) was added to a mixture of syrupy phosphoric acid (5 ml.) and phosphorus pentoxide (5 g.) at 120°C. The compound melted and after about 20 seconds an orange solid separated. The temperature was raised to 150°C. for 3 mins. and the mixture cooled and 30 ml. water added. The orange coloured solid was filtered.

Yield = 0.9 g.

M.p. = 209-211°C.

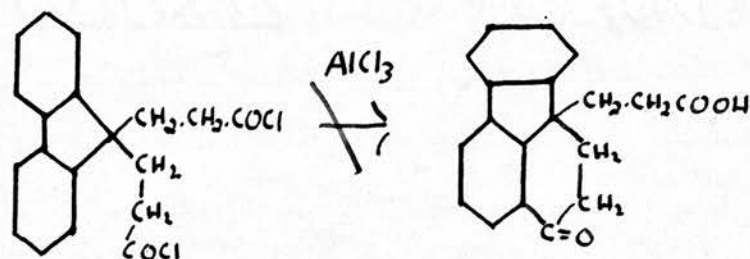
Mixed m.p. with the anhydride of 3:3'-diphenylene-2-carboxyvinylacetic acid (p. 110) of m.p. 212-213°C. was 211-212°C.

Discussion on Experimental Results.

The preparation of the catalyst trimethylbenzylammonium hydroxide was the first step in the investigation of the condensation of acrylonitrile with fluorene and its derivatives. The isolation of trimethylbenzylammonium chloride (p. 28) presented some difficulties due to the solubility of product and the extreme volatility of the trimethylamine, but the most effective method found was the passing of the trimethylamine into cooled benzyl chloride until no more trimethylamine could be absorbed by the semi-solid mixture of benzyl chloride and trimethylbenzylammonium chloride. The action of potassium hydroxide on quaternary ammonium salts gives an equilibrium mixture of the two reactants, the quaternary ammonium hydroxide and potassium chloride. Therefore the reaction had to be done in a medium where the potassium chloride was precipitated. Methanol proved effective in this respect, so that the production of the trimethylbenzylammonium hydroxide went almost to completion. The solution of the hydroxide in the methanol proved a very effective catalyst for condensing acrylonitrile with fluorene (p. 29) to produce the bis-9:9'-(2-cyanoethyl)-fluorene/

fluorene, as found by Bruson and co-workers (J.A.C.S., 1942, 64, 2457). This product, following Bruson's work was hydrolysed with ease to the bis-9:9'-(2-carboxyethyl)-fluorene (p. 30). The diethyl ester was obtained by adding ethanol to the diacid chloride, formed by refluxing the diacid with thionyl chloride.

The acid chloride was treated with a mono-molecular quantity of anhydrous aluminium chloride in light petroleum in the expectation that cyclisation might take place with one of the propionyl chloride side chains, but subsequent treatment gave only the original acid in fairly high yield (p. 31).



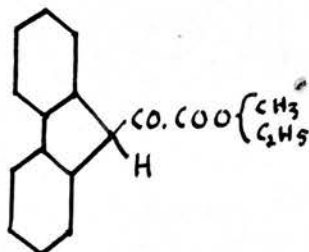
Cyclisations with sulphuric acid of varying strengths were tried (p. 31) on the diacid but either the original acid or a product completely soluble in water resulted. It was concluded that sulphuric acid concentrated enough and in sufficiently vigorous conditions to cyclise the acid, sulphonates the fluorene ring system.

The/

The cyclisation method involving catalytic amounts of anhydrous zinc chloride in glacial acetic acid and acetic anhydride also proved ineffective, the original acid being returned.

It was decided to discard this method of synthesising fluoranthene derivatives, and investigate the possibility of condensing 9-monosubstituted fluorene with acrylonitrile to discover if a single 9-propionic acid side chain in the fluorene molecule would be more amenable to cyclisation.

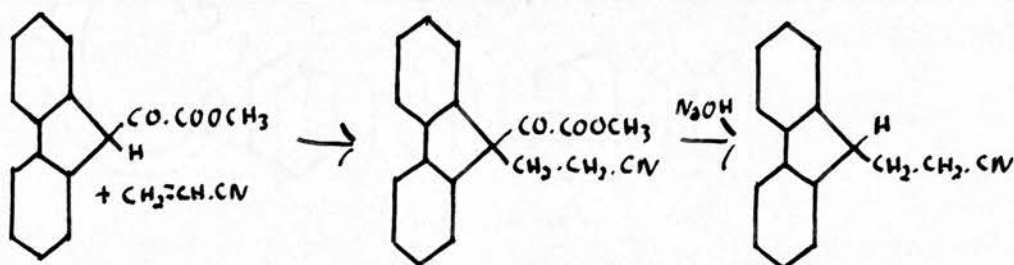
The first compounds prepared were the ethyl and methyl 1-keto-1'-(9-fluorenyl) acetates.



The preparation of the ethyl ester (p. 32) according to Wislicenus and Thiele (Ber., 1900, 33, 771, 852) was not very satisfactory due to the difficulty of obtaining good yields of the compound in a pure stable crystalline form. However the production of the methyl ester according to Kuhn and Levy (Ber., 1928, 41, 2243) was satisfactory, though the yields were not high. The melting-point obtained by Kuhn and/

and Levy for this compound is quoted as uncorrected and the melting-point of our product was found to be 10°C. higher.

Condensation of this compound with acrylonitrile followed by treatment with sodium hydroxide solution would have given 9-fluorenyl-2-propionitrile as follows.



However the condensation could not be effected (p. 35), due in all probability to the enolisation of the compound destroying the alkalinity of the catalyst, trimethylbenzylammonium hydroxide.

The preparation of fluorene-9-carboxylic acid (p. 36) by treatment with solid carbon dioxide of sodium fluorene (prepared by the action of sodamide on a melt of fluorene) produced such a small yield of the acid that further investigation of this compound was unwarranted. The small yield of the acid was probably due to a small yield of the sodium fluorene, the reaction between fluorene and sodamide probably needing an autoclave.

The/

The condensation of other fluorene derivatives with acrylonitrile was next attempted.

The preparation of 9-fluorenone (p. 37) by the method of Huntress, Hersberg and Cliff (J.A.C.S., 1937, 53, 2720) went smoothly, but its reduction to 9-fluorenol (p. 38) with zinc and ammonium hydroxide presented many difficulties.

Werner and Grab (Ber., 1904, 30, 2896) gave details for this reduction in which large quantities of ammonium hydroxide were used. We found that the product did indeed melt at the quoted melting-point for fluorenol, but subsequent reactions of 9-fluorenol were not given by this product. Moreover an authentic sample of 9-fluorenol depressed the melting-point of this product. A search of the literature showed that Bachmann (J.A.C.S., 1933, 55, 1185) had found that a complex of fluorenol and fluorenopinacol gives the same melting-point as fluorenol, and this was probably the product claimed by Werner and Grab. On modifying the procedure, however, by keeping fluorenone and its reduction products in solution throughout the reaction 9-fluorenol was obtained.

The preparation of 9-chlorofluorene (p. 41) according to Schlenk and Bergmann (Ann., 1928, 463, 173/

172) went as reported, but the product could not be condensed with acrylonitrile. 9-Ethylfluorene (p.42) was obtained by the action of ethyl magnesium iodide on 9-chlorofluorene, following the method of Miller and Bachmann (J.A.C.S., 1935, 57, 771) but the percentage yields of the two products proved to be the reverse of those obtained by the Americans. The attempt to condense the impure 9-ethylfluorene with acrylonitrile was unsuccessful.

Attempts to prepare 9-methylfluorene were unaccountably unsuccessful. The first stage in its preparation according to Wislicenus and Densch (Ber., 1902, 35, 762) was a condensation between methyl-1-keto-1'-(9-fluorenyl) acetate and methyl iodide in presence of potassium ethoxide in ethanol, but no reaction took place and the starting material was returned, even after much precautions as preparing dried alcohol were observed.

An attempt to reduce 9-methylfluorenol (p. 44) prepared by the method of Daufresne (Bl., 4, 11234) to the 9-methylfluorene by the method of Wanscheidt and Moldavski (Ber., 1931, 64, 917) was unsuccessful for no apparent reason. The conditions given for this reduction are similar to those given for the reduction of 9-benzyl- and 9-phenyl-fluorenols which were found to/

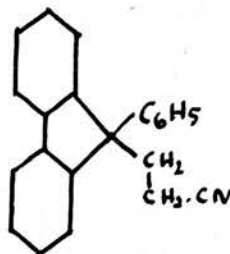
to undergo readily this reduction to the corresponding fluorenes. Other methods of reduction (p. 45) were tried, including refluxing with phosphorus and hydriodic acid but these were also unsuccessful. It was thought that these results might be due to the starting material but the analyses of a sample of the 9-methyl-fluorenol were reasonably good, and the melting-point was sharp.

9-Benzylfluorenol was prepared (p. 45) by a Grignard synthesis from fluorenone but in rather poor yields. This was due to the difficulty of preparing the benzyl magnesium chloride because of deposition of the Grignard reagent on the surface of the unreacted magnesium. As has been stated the reduction of the 9-benzylfluorenol to the 9-benzylfluorene by the method of Wanscheidt and Moldavski went readily in good yields (p. 46), but the 9-benzylfluorene would not condense with acrylonitrile.

It was found that in contrast to 9-chloro-fluorene, 9-ethylfluorene and 9-benzylfluorene, 9-phenylfluorene condensed with acrylonitrile. A possible explanation of this is that the chlorine atom, and the substituent alkyl groups in the 9-position of the fluorene molecule deactivate the otherwise/

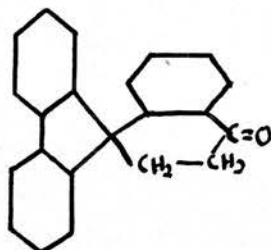
otherwise labile hydrogen atom, whereas with the aryl substituent it retains its activity as the 9-carbon atom is still completely in contact with cyclic structures.

This condensation went well in dioxan to give 9-phenyl-9'-(2-cyanoethyl) fluorene (p. 50). A larger scale experiment in benzene was also successful and a larger yield of as pure a product was obtained with a simpler method of isolation. The nitrile was also hydrolysed in aqueous ethanolic sodium hydroxide solution to the corresponding acid, 9-phenyl-9'-(2-carboxyethyl) fluorene, which gave a poor analysis result but which was satisfactorily characterised by its methyl ester.

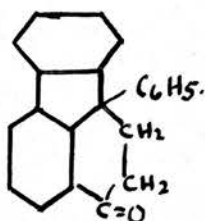


The acid was cyclised (p. 53) by the acid chloride, Friedel-Crafts method, but only a poor yield of an analytically impure ketone, 4-keto-1-phenyl-1:2:3:4-tetrahydrofluoranthene, was obtained. This ketone was characterised by the formation of a dinitrophenylhydrazone. However the ketone formed was not necessarily the 4-keto-1-phenyl-1:2:3:4-tetrahydrofluoranthene because cyclisation could take place/

place on the phenyl group giving the following spirane compound.



instead of the fluoranthene derivative as follows.



As the ketone was only obtained in small yield and as it was hoped that anhydrous hydrogen fluoride would be available for further attempts at cyclisation, oxidation experiments to prove the structure were not attempted.

Condensation of acrylonitrile with 9-fluoreno1.

(Note: For formulæ of compounds and their reactions see Flowsheet

When acrylonitrile was added to a solution of 9-fluoreno1 in dioxan containing trimethylbenzyl-ammonium hydroxide in catalytic amounts heat was evolved showing that a reaction was taking place (p. 56). From analysis it was found that a molecular amount of the acrylonitrile condensed with the 9-fluoreno1, though the best yields of the product were obtained when bimolecular amounts were used in the reaction. Bruson and Reiner (J.A.C.S., 1943, 65, 24) have stated that acrylonitrile condenses with monohydric unsaturated alcohols, cyclic alcohols, and ether alcohols to form cyanoethyl ethers, but subsequent reactions of our product showed that no ether formation occurred, the hydrogen in the 9-position of the 9-fluoreno1 having retained its reactivity and taken part in the condensation. The product of the reaction was an oil which decomposed on attempted vacuum distillation, but from which a solid could be obtained. The solid analysed well for 3:3'-diphenylene-3"-hydroxybutyronitrile (2) and the uncrystallisable oil was found by further reactions to consist essentially of this compound. The solid (p. /

(p. 61) and the oil (p. 57) were both hydrolysed by refluxing with sodium hydroxide to give in only fair yields, the unsaturated acid 3:3'-diphenylenevinyl-acetic acid (4). The unsaturated nature of this acid was shown by the ease with which it brominated to give the dibromo-derivative 3:3'-diphenylene-2-3"-dibromobutyric acid (6)(p. 63). It was expected that treatment with zinc and glacial acetic acid (p. 64) would remove bromine from this compound and reduce it to 9-fluorenyl-2-propionic acid (7), but the compound obtained was identified with 3:3'-diphenylene-3"-butyro- γ -lactone (5) which was obtained by refluxing the unsaturated acid (4) with sulphuric acid (p. 66). However the 9-fluorenyl-2-propionic acid (7) was obtained by the catalytic hydrogenation of the unsaturated acid (4) with Adams brown platinum oxide (p. 65) and also by the reduction of the γ -lactone (5) with hydriodic acid and red phosphorus following the method of Rupe and Steinbeck (Ber., 1911, 44, 584) for the saturation of β - γ -unsaturated carboxylic acids.

A feature of all these reactions was the poor yields of pure products due to the formation of tarry byproducts in the reactions. This was probably due to other reactions taking place at the site of the 2:3 double bond or the 3-hydroxyl group. The extreme reactivity and rather peculiar nature/

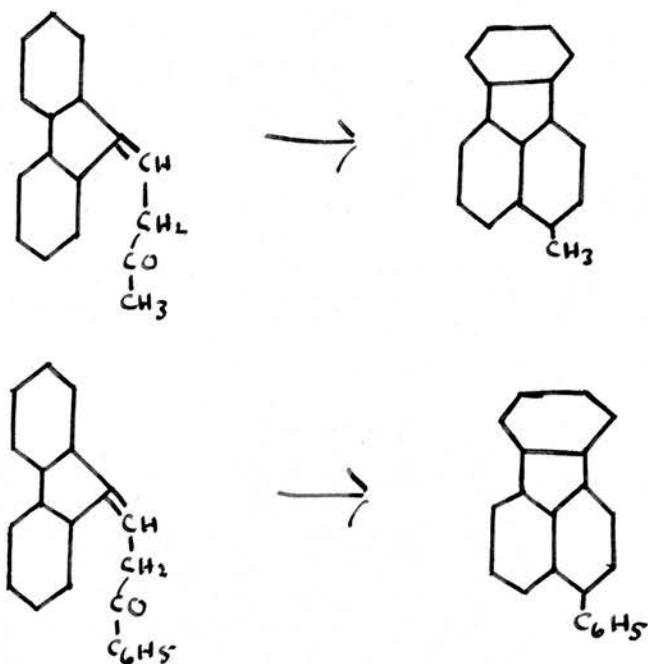
nature of these groups were found in experiments on the lactone and on the initial products of the condensation. All attempts to obtain the hydroxy acid from the lactone were unsuccessful. The lactone (5) was precipitated from cold alkaline solution by acids even when only a slight excess of acid was present. It was expected from the initial hydrolysis of the hydroxynitrile (2) that the unsaturated acid might be obtained by refluxing the lactone for some time with sodium hydroxide solution and then acidifying but again the lactone was obtained. A possible explanation of this fact was that water was removed from the hydroxynitrile before hydrolysis took place, leaving the unsaturated nitrile (3). This explanation, however, had to be discarded because an attempt was made to hydrolyse the unsaturated nitrile (3:3'-diphenylenevinylacetonitrile)(3) with sodium hydroxide solution, but even on a small scale experiment ammonia was still being evolved even after 30 hours' refluxing. However fluorene was found to have sublimed into the condenser, and this was the only pure crystalline product isolated from this experiment (p. 63). The possible explanation of this reaction is that water under alkaline catalysis splits the double bond with the formation of fluorene and the hydroxypropionitrile/

nitrile. Thus the possible mechanism of the initial hydrolysis of the 3:3'-diphenylene-3"-hydroxybutyronitrile (2) to the 3:3'-diphenylenevinylacetic acid (4) is that the nitrile is first hydrolysed to the amide which loses water to give the unsaturated amide which undergoes further hydrolysis to the unsaturated acid (4).

Other peculiar reactions were observed with the original hydroxynitrile (2). On refluxing both the oil (p. 59) and the solid (p. 60) with hydrochloric acid, a mixture of the unsaturated nitrile (3) and the γ -lactone (4) was obtained. The separation of these was found to be very simple as hot light petroleum extracted the nitrile leaving the lactone. This meant that water must have been removed from the 2:3-position in the original hydroxynitrile (2) to form the unsaturated nitrile (3). The unsaturated nitrile could not have been present in the original oil because nothing could be extracted from this by light petroleum, which should have been the case had any of the unsaturated nitrile been present. The formation of the lactone (5) was explained by experiments showing that the unsaturated nitrile when refluxed with hydrochloric acid (p. 62) or with a mixture of glacial acetic and hydrobromic acids/

acids (p. 61) hydrolysed and formed the lactone in good yield.

Following the method of Hauser, Humphlett and Weiss (J.A.C.S., 1948, 70, 426) for the preparation of ketones from nitriles, with Grignard reagents, attempts were made to form the two following unsaturated ketones (p. 60) which might be cyclised by the method of France, Tucker and Forrest (J.C.S., 1945,7) to give 4-methyl and 4-phenylfluoranthenes.



However the 3:3'-diphenylene-3"-hydroxybutyronitrile (2) did not react with either phenyl magnesium bromide or methyl magnesium iodide (p. 62) and the only products obtained were those which were obtained by refluxing the hydroxynitrile with hydrochloric acid. The/

The unsaturated nitrile also did not react with methyl magnesium iodide (p. 62).

The attempt to cyclise the unsaturated acid 3:3'-diphenylenevinylacetic acid to 4-hydroxyfluoranthene with acetic anhydride containing sodium acetate was unsuccessful (p. 68).

As has been stated the 9-fluorenyl-2-propionic acid (7) was obtained though only in poor yield. The yield of this acid obtained in this work was 23% starting from fluorene, which is a good improvement on von Braun's synthesis (Ber., 1929, 62, 148) in which he obtained yields of between 5 and 8% of this acid from fluorene-9-carboxylic acid, a compound only obtained in a yield of 8% from fluorene in this work.

Following up von Braun's work the 9-fluorenyl-2-propionic acid was cyclised (p. 69) by the acid chloride - Friedel-Crafts method, and a rather impure product was obtained, though a small quantity of the solid, 4-keto-1:2:3:4-tetrahydrofluoranthene (8), whose melting-point agreed well with that of von Braun, was obtained after a chromatographic separation. The yields here were not as good as those of von Braun but that might be explained by the fact that the acid chloride was not distilled to get it into/

into a pure state before treatment with anhydrous aluminium chloride. The 4-keto-1:2:3:4-tetrahydrofluoranthene was further characterised by the preparation of a dinitrophenylhydrazone (p. 72).

The oil containing some of the ketone was next reduced by the Clemmensen method to 1:2:3:4-tetrahydrofluoranthene (9) and the impure product was dehydrogenated by chloranil (p. 73) to give fluoranthene (10). The fluoranthene was separated from oily impurities by the formation of its picrate, which did not depress the melting-point of an authentic sample of fluoranthene picrate. The fluoranthene was separated from the picrate, and did not depress the melting-point of an authentic sample of fluoranthene. However the synthesis of fluoranthene as conducted in this work was not done with exceptional care and larger yields would probably have been obtained had the products been purified at each stage. As it was expected that anhydrous hydrofluoric acid would be available for further cyclisation experiments, no attempts were made to improve this method of cyclisation.

As/

As Bruson (J.A.C.S., 1942, 64, 2457) had effected the condensation of allylnitrile and crotonitrile with fluorene to form the bis-9:9'-(2-cyanoisopropyl) fluorene, it was thought that the phenyl derivative of acrylonitrile (cinnamitrile) should also undergo a similar condensation with fluorene, to give 9-(2-cyanophenylethyl) fluorene, and this was found to be the case.

The cinnamitrile was prepared by the dehydration of the amide of cinnamic acid. A new large scale method (p. 75) for the production of the amide was evolved, using thionyl chloride to convert the cinnamic acid to the acid chloride, removing the thionyl chloride under reduced pressure, before distilling the cinnamyl chloride. The acid chloride was dissolved in dried ether and ammonia gas passed into the solution. It was expected that the amide would remain in solution and the ammonium chloride formed in the reaction be precipitated, but it was found that both the amide and the salt came out of the ether. It was also found that on treatment of this precipitate with water some of the cinnamic acid was regenerated, but the addition of ammonium hydroxide to the water was effective in removing the acid to leave the almost pure cinnamamide. The amide was dehydrated by refluxing with thionyl chloride/

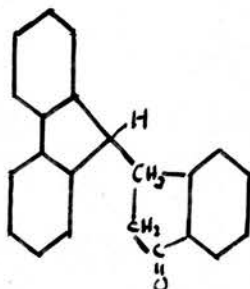
chloride, the excess thionyl chloride distilling under reduced pressure before the cinnamitrile formed in the reaction. The nitrile at this stage was definitely acidic, and as it was to be used with an alkaline catalyst, all the contaminating acids had to be removed by treatment with potassium carbonate solution. Yields in both stages of the preparation were reasonably good.

The condensation of the cinnamitrile with fluorene (p. 77) was found to take place when the reaction was carried out in dioxan solution at the temperature of a steam bath. Lower temperatures did not prove effective, for when dioxan was not available, the experiment was attempted in refluxing benzene, but the only solid product obtained was the unchanged fluorene. However when carried out in toluene, with a larger amount of catalyst at the temperature of the steam-bath, the 2-phenyl-2'-(9-fluorenyl) propionitrile was isolated by a more direct method and in better yields than with dioxan. A certain amount of tarry product, removed by treatment with charcoal, was obtained in the reaction. This was to be expected with a styryl compound in the presence of a polymerising agent, and may also account for the moderate yields of the required product/

product.

The hydrolysis of the nitrile to the acid (p. 79) proved to be a little troublesome as the amide, identified by the preparation of a sample from the acid (p. 81) was formed during the reaction and did not appear to be hydrolysed readily. A yield of about 30% of this amide was isolated after refluxing the nitrile in aqueous ethanolic sodium hydroxide solution for 20 hours. A small amount of the amide (2 g.) required 30 hours for complete hydrolysis to the acid in a similar medium. However yields of the hydrolysis product 2-phenyl-2'-(9-fluorenyl)-propionic acid were almost theoretical and analysis of the acid was very good. The acid was characterised by its methyl ester which also analysed satisfactorily. The acid was cyclised by the acid chloride, Friedel-Crafts method to give a ketone, characterised by its dinitrophenylhydrazone. Though a good yield of solid product was obtained only a few milligrams of a pure crystalline compound, which gave poor analytical figures for the suspected 4-keto-2-phenyl-1:2:3:4-tetrahydrofluoranthene (p. 82) were finally obtained. There is, however, another possibility for this cyclisation, as it may have taken place onto the phenyl/

phenyl group giving the ketone 1-(9-fluorenyl)-hydrindone-3.



However again as the ketone was only obtained in small yield and it was hoped that anhydrous hydrogen fluoride would be available for further attempts at cyclisation, oxidation experiments to prove the structure were not attempted.

The/

The Stobbe Reaction on 9-fluorenone (p. 92, etc.).

(Note: For formulae of compounds obtained and the equations of their reactions, see Flowsheet

The alkoxide catalysed condensation of diethyl succinate with fluorenone was initially attempted by the method given by Johnson, Peterson and Schneider (J.A.C.S., 1947, 69, 74) for benzophenone, and the expected b-monoethyl ester, 3:3'-diphenylene-2-carbethoxyvinylacetic acid (I, p. 103) was obtained along with a small amount of the 'dicondensation product', 1:4-bisdiphenylene-2:3-dicarboxybutadiene (A, p. 94) and an oil which hydrolysed to give the dicarboxylic acid, 3:3'-diphenylene-2-carboxyvinylacetic acid (II, p. 104). Some unchanged fluorenone was also obtained, but if a longer reaction time than 30 minutes was allowed, then there was a decrease in the yield of the monoethyl ester, and an increase in the yield of the dicondensation product. Also if refluxing was continued for 2 hours then the only separable crystalline solid even after hydrolysis was the dicondensation product and this in very poor yields. Refluxing for less than 30 minutes produced more unchanged fluorenone, and subsequently a smaller yield/

yield of the b-monoethyl ester. It is thus clear that the method is somewhat capricious.

The original method given by Stobbe (Ann., 1894, 282, 281; 1899, 308, 89) was then tried (p.92) but only a relatively small yield of the 'dicondensation product' was obtained.

The experiments of Stobbe (p. 88) and Johnson (p. 90) on benzophenone were repeated and the results comparable to those obtained by these workers were obtained. The yields obtained by the Johnson method was poorer than that quoted but the experiment was not carried out in an atmosphere of nitrogen which Johnson states is essential for high yields of pure products. However the expected improved yield of the b-monoethyl ester was not obtained when the condensation with fluorenone was repeated in an atmosphere of nitrogen. The results were exactly the same as those obtained when oxygen was not excluded from the apparatus.

Thus the experiment quoted (p. 101) had to be accepted as the best possible for the preparation of the 3:3'-diphenylene-2-carbethoxyvinylacetic acid.

The elucidation of the structure of the product known as the 'dicondensation product', 1:4-bis-diphenylene-2:3-dicarboxybutadiene (A), first presented/

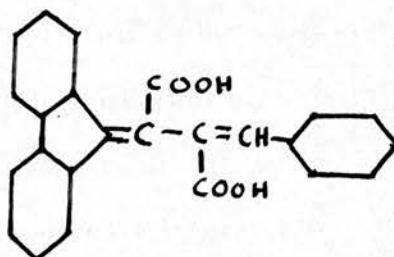
presented great difficulty, as all that was known about it was that it gave a sodium salt insoluble in cold water, but soluble in large volumes of boiling water, and that the acid could be precipitated by acidification of the boiling solution. Also the production of an alkaline insoluble compound by the action of a mixture of hydrobromic and glacial acetic acids, later taken to be the di- γ -lactone (C) from which the diacid could be regenerated by refluxing for some time with sodium hydroxide solution, was of little use, as was the inability to form by ordinary methods, an anhydride or an ester of the acidic product.

However the rather inaccurate molecular weight determinations (p. 101) suggested a dicondensation product of the diethyl succinate and two molecules of fluorenone, and the production of a dimethyl ester (B, p. 95) with diazomethane was a distinct help. The decarboxylation of the acid by copper bronze in quinoline (p. 98) to 1:4-bisdiphenylenebutadiene (C) and the two stage reduction of this compound (Wislicenus, Ber., 1915, 48, 622) through 1:4-bisdiphenylenebutene (D), to 1:4-bisdiphenylenebutane (E) with the melting-points of these compounds (p. 100) corresponding to those obtained by Wislicenus, was adequate proof/

proof of the 'dicondensation product' being 1:4-bisdiphenylenebutadiene. The yield in the decarboxylation experiment was reasonably good considering the rather vigorous conditions, and the reductions following the instructions of Wislicenus were also satisfactory.

The b-monoethyl ester (3:3'-diphenylene-2-carbethoxyvinylacetic acid, I) was readily esterified (p. 109) to give the diethyl (III) and methyl ethyl (IV) esters. The diethyl ester condensed with benzaldehyde (p. 125) to give a compound identified as 1-(9-fluorenylidene)-2-benzylidenesuccinic acid also prepared by the method given by Stobbe (Ann., 1911, 380, 126).

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This proved the existence of an α -methylene group in the diethyl ester and so in the b-monoethyl ester(I). The b-monoethyl ester was also easily hydrolysed (p. 104) to the dibasic acid, 3:3'-diphenylene-2-carboxyvinylacetic acid (II), which could be reduced (p. 111) to 4-fluorenylsuccinic acid (V), whose diethyl/

diethyl ester was identified with diethyl 9-fluorenylsuccinate, prepared in another way. This showed the fundamental structure of the initial condensation product. The 9-fluorenylsuccinic acid (p. 85) was prepared by the method of Alder, Pascher and Vagt (Ber., 1942, 75B, 1151) who isolated this compound as the anhydride. As the paper of Alder and his co-workers was not available when the experiment was carried out, an abstract of the paper was used (Chem. Abstracts, 1944, 1248). Consequently our method differed in detail from that of the German authors, and whereas they isolated the anhydride, we isolated the acid. As the acid was soluble to a certain extent in water, the method of isolation used was not conducive to exceptional purity and yields. The results of the experiment are similar to those of Alder and his co-workers, who also obtained some unidentified material. The melting-points of the diethyl ester and the anhydride of the 9-fluorenylsuccinic acid, samples of which were prepared, compare favourably with those obtained by Alder.

The anhydride was obtained by two methods, both being attempts at cyclisation. One was the treatment of the acid with syrupy phosphoric acid and phosphorus pentoxide (p. 87) and the other an acetic/

acetic anhydride-glacial acetic acid treatment (p. 86). All other attempts at cyclisation were unsuccessful.

The diacid (3:3'-diphenylene-2-carboxyvinyl-acetic acid, II) did not give a satisfactory melting-point, a certain discoloration and softening being observed a few degrees before the compound finally melted. The explanation of this phenomena lies in anhydride formation, as the anhydride of the acid melts just a few degrees higher than the acid itself and does not depress the melting-point of the acid but actually raises it.

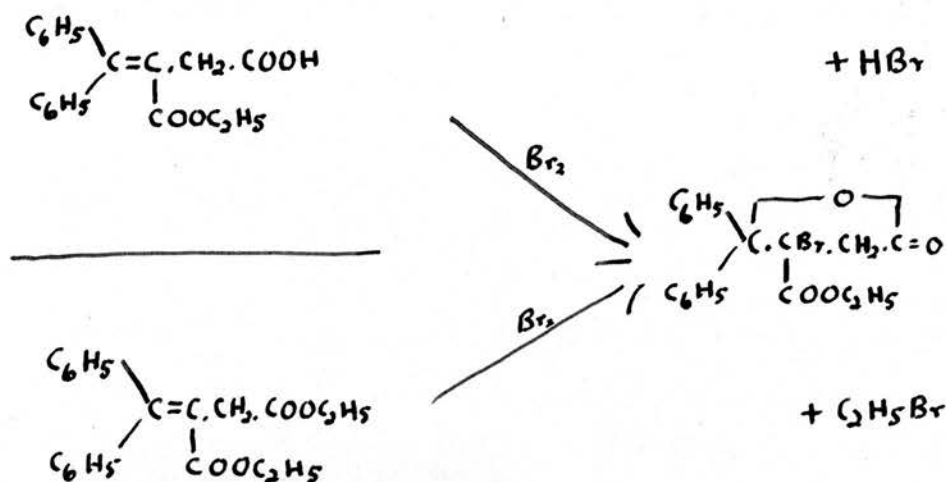
The anhydride (VI) of the acid was formed easily and in good yield from several sources. It was formed by the action of acetyl chloride on the diacid (p. 110), by the action of syrupy phosphoric acid and phosphorus pentoxide, and the action of an acetic anhydride, glacial acetic acid mixture on the b-monoethyl ester (I)(p. 110). The last two experiments were unsuccessful attempts at cyclisation. The anhydride was also formed when the melts of the a-monoethyl and a-monomethyl esters were raised above 150°. These two esters, ethyl 3:3'-diphenylene-2-carboxyvinylacetate (VII) and methyl

3:3'-diphenylene-2-carboxyvinylacetate (VIII) were obtained by the esterification of the dibasic acid (II) in the alcohol containing concentrated sulphuric acid (p. 107). A prolonged reaction time was necessary (24 hours) and with ethanol a mixture of the diethyl and a larger quantity of the α -monoethyl esters was obtained, whereas with methanol only the α -monoethyl ester was obtained.

These experiments show the relative unreactivity of the β -carboxyl group when compared to the α -carboxyl group. The explanation of the formation of some of the diethyl ester with ethanol when no trace of a dimethyl ester was obtained might be that in the case of ethanol the conditions of refluxing are slightly more vigorous due to the difference in boiling points of ethanol and methanol.

The proof of the position of the esterified carboxyl group in the mono-ethyl esters was obtained by bromination experiments. It was thought at first that bromination of the original condensation product the β -monoethyl ester (p. 115) would give rise to a dibromo compound showing the existence of the double bond but analysis showed that only one bromine atom was present in the resulting bromo compound, even though molecular equivalents of bromine/

bromine had been used. This fact, the fact that the resulting compound, obtained easily and in good yield was non-acidic, being insoluble in potassium carbonate solution, and the fact that fumes of hydrobromic acid were given off during the reaction, were evidence that a somewhat unexpected reaction was taking place, and recalled the observation of Stobbe (Ber., 1911, 44, 1297) that he obtained the 3:3'-diphenyl-2-bromo-paraconic acid ethyl ester (3:3'-diphenyl-2-carbethoxy-2'-bromobutyro-γ-lactone) by the bromination of the b-monoethyl and diethyl esters of 3:3'-diphenyl-itaconic acid (3:3'-diphenyl-2-carbethoxyvinylacetic acid and its ethyl ester) as follows.



The/

The bromination was therefore repeated on the diethyl ester (III) (ethyl-3:3'-diphenylene-2-carbethoxyvinyl acetate) when the same compound was obtained in equally good yield as with the monoethyl ester (p. 116). The bromo-compound was therefore 3:3'-diphenylene-2-carbethoxy-2'-bromobutyro- γ -lactone (IX).

Following up Stobbe's work the diacid (3:3'-diphenylene-2-carboxyvinylacetic acid, II) was also brominated (p. 112) when an impure sample of the 3:3'-diphenylene-2-carboxy-2'-bromobutyro- γ -lactone (X) was obtained in poor yield. The same compound was obtained when the mono-esterification product of the diacid (ethyl-3:3'-diphenylene-2-carboxyvinyl acetate, VII), but in improved yield and purity (p. 113).

The fundamental structure of these bromine compounds was exhibited by their reaction on treatment with zinc and glacial acetic acid. The 3:3'-diphenylene-2-carboxy-2'-bromobutyro- γ -lactone (X) lost bromine and was reduced in good yield to 9-fluorenylsuccinic acid (V). 3:3'-Diphenylene-2-carbethoxy-2'-bromobutyro- γ -lactone (IX) also lost bromine and was reduced to 3:3'-diphenylene-2-carbethoxybutyric acid (XI)(p. 122), also obtained by the reduction of the original b-monoethyl ester (I)/

(I) with zinc and glacial acetic acid (p. 120). This compound was hydrolysed to 9-fluorenylsuccinic acid, and was esterified in methanol to methyl 3:3'-diphenylene-2-carbethoxybutyrate (XII), also obtained by the reduction of methyl 3:3'-diphenylene-2-carbethoxyvinyl acetate (IV) with zinc and glacial acetic acid (p.121).

The hydrolysis of the 3:3'-diphenylene-2-carbethoxy-2'-bromobutyro- γ -lactone (IX), both by a mixture of glacial acetic and hydrobromic acids, and by sodium hydroxide solution, produced an unexpected result in that bromine was removed. The compound formed was not precipitated immediately from alkaline solution on acidification but gradually separated out in a crystalline form, and so was not expected to be a dibasic acid but was in fact the 3:3'-diphenylene-2-carboxybutyleno- γ -lactone (XIII). The same compound was obtained by treating the 3:3'-diphenylene-2-carboxy-2'-bromobutyric- γ -lactone (X) with sodium hydroxide solution (p. 117).

The unsaturated and lactonic nature of this compound was further shown by the heating of the 3:3'-diphenylene-2-carbethoxy-2'-bromobutyro- γ -lactone (IX) with pyridine (p. 119) when hydrogen bromide was removed and a neutral compound insoluble in alkali was obtained in good yield. This was the 3:3'-diphenylene/

diphenylene-2-carbethoxybutyleno- γ -lactone (XIV) which on hydrolysis with sodium hydroxide solution (p. 119) gave a compound identified with the 3:3'-diphenylene-2-carboxybutyro- γ -lactone (XIII).

This compound was also reduced (p. 118) by zinc and glacial acetic acid to a good yield of a compound identified with 9-fluorenylsuccinic acid (V).

The expected decarbethoxylation of the 3:3'-diphenylene-2-carbethoxyvinylacetic acid (I) proceeded according to Johnson, Goldman and Schneider (J.A.C.S., 1945, 67, 1357) on refluxing with a glacial acetic acid and hydrobromic acid mixture (p. 124). The product separated was identified with the 3:3'-diphenylene-butyro- γ -lactone (XV) previously prepared (p. 66) and discussed (p. 13). The compound separated was also reduced (p. 124) by means of phosphorus and hydriodic acid to 9-fluorenyl-2-propionic acid (XVI) giving further proof that the lactone had been obtained.

Further attempts at cyclising the 3:3'-diphenylene-2-carbethoxyvinyl acetic acid were made. The acid chloride, and Friedel-Crafts method was attempted but was invariably unsuccessful. The Borsche/

Borsche method (Ann., 1936, 524, 9) which was found to be very successful with the 3:3'-diphenyl-2-carbethoxyvinylacetic acid (p. 91) in which the b-monoethyl ester (I) was refluxed in acetic anhydride, containing sodium acetate, was very promising in that a neutral product was obtained. Attempts to separate a pure crystalline compound were unsuccessful. In one of several experiments a few milligrams of a pure crystalline product was obtained, but as this could not be repeated the method had to be discarded.

SUMMARY

Two new methods have been evolved for the preparation in improved yields of 9-fluorenyl-2-propionic acid, from which fluoranthene has been synthesised, thus confirming the work of von Braun.

The first of these methods resulted from investigations of the trimethylbenzylammonium hydroxide catalysed condensation of acrylonitrile with 9-substituted fluorenes, the initial condensation in the preparation of the above acid being with 9-fluorenol. Acrylonitrile was also condensed with 9-phenylfluorene, and the product hydrolysed to an acid cyclisable to a ketone, but acrylonitrile could not be condensed with 9-chloro-, 9-ethyl, and 9-benzylfluorenes, nor with 1-keto-1' (9'-fluorenyl) acetic acid.

The first step in the second method was an alkoxide catalysed condensation of diethylsuccinate and 9-fluorenone (a Stobbe reaction). An intensive study was made of this reaction, so that the structure of its various products could be firmly established. These were found to be the mono-condensation products, 3:3'-diphenylene-2-carbethoxyvinylacetic acid and the dibasic acid, 3:3'-diphenylene-2-carboxyvinylacetic acid whose structures were established by esterification, hydrolysis, reduction and bromination experiments/

experiments, and the dicondensation product 1:4-bisdiphenylene-2:3-decarboxybutadiene whose structure was elucidated by decarboxylation to the known hydrocarbon. Reduction of the lactone produced by the decarboxylation of the mono-condensation products gave the 9-fluorenyl-2-propionic acid.

It was found that fluorene condensed with molecular amounts of cinnamnitride (phenylacrylonitrile) under the catalytic action of trimethylbenzylammonium hydroxide and the product hydrolysed to an acid cyclisable to a ketone.

It was also found that the 9-fluorenyl-2-propionic acid, and the substituted 9-fluorenyl-2-propionic acids prepared, were very resistant to cyclisation, the only method from which crystallisable products were obtained being acid chloride-Friedel-Crafts methods.

POSTSCRIPT.

The author wishes to record his appreciation of the privilege enjoyed by him in working under the direction of Dr. Neil Campbell, and to thank Dr. Campbell for his constant interest, and most helpful advice given, during this work.

He also wishes to thank W.K. Buchanan, B.Sc. for a sample of 1-(9-fluorenylidene)-2-benzylidene-succinic acid.

Thanks are also due to the University of Edinburgh for the award of the Gray Scholarship during whose tenure most of this work was carried out.

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This shows diagrammatically the reactions involved and the compounds obtained in the study of

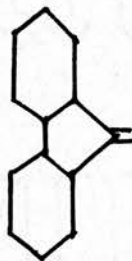
- (1) The condensation of acrylonitrile and 9-fluorenol..(p. i)
(2) The Stobbe Condensation on 9-fluorenone..... (pp.ii,iii,iv)

Page ii shows the initial condensations and the derivatives obtained from the 'dicondensation product'.

Page iii shows the esterification, hydrolysis, and reduction derivatives of the 'monocondensation product'.

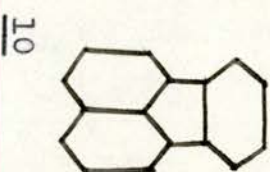
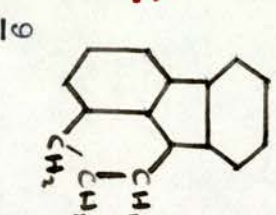
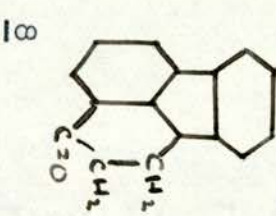
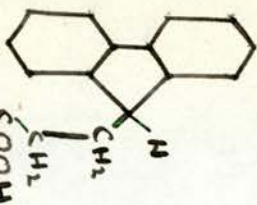
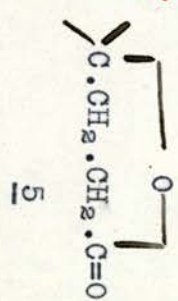
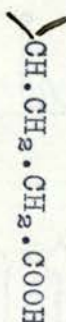
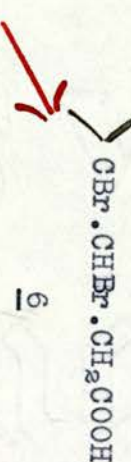
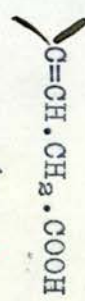
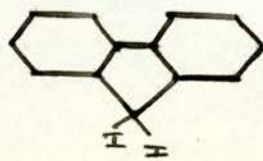
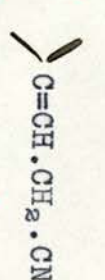
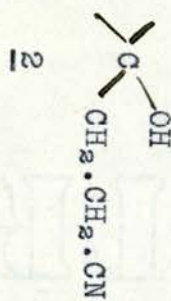
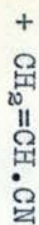
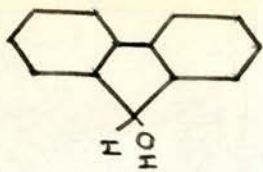
Page iv shows the compounds obtained by bromination of the monocondensation derivatives and their reactions.

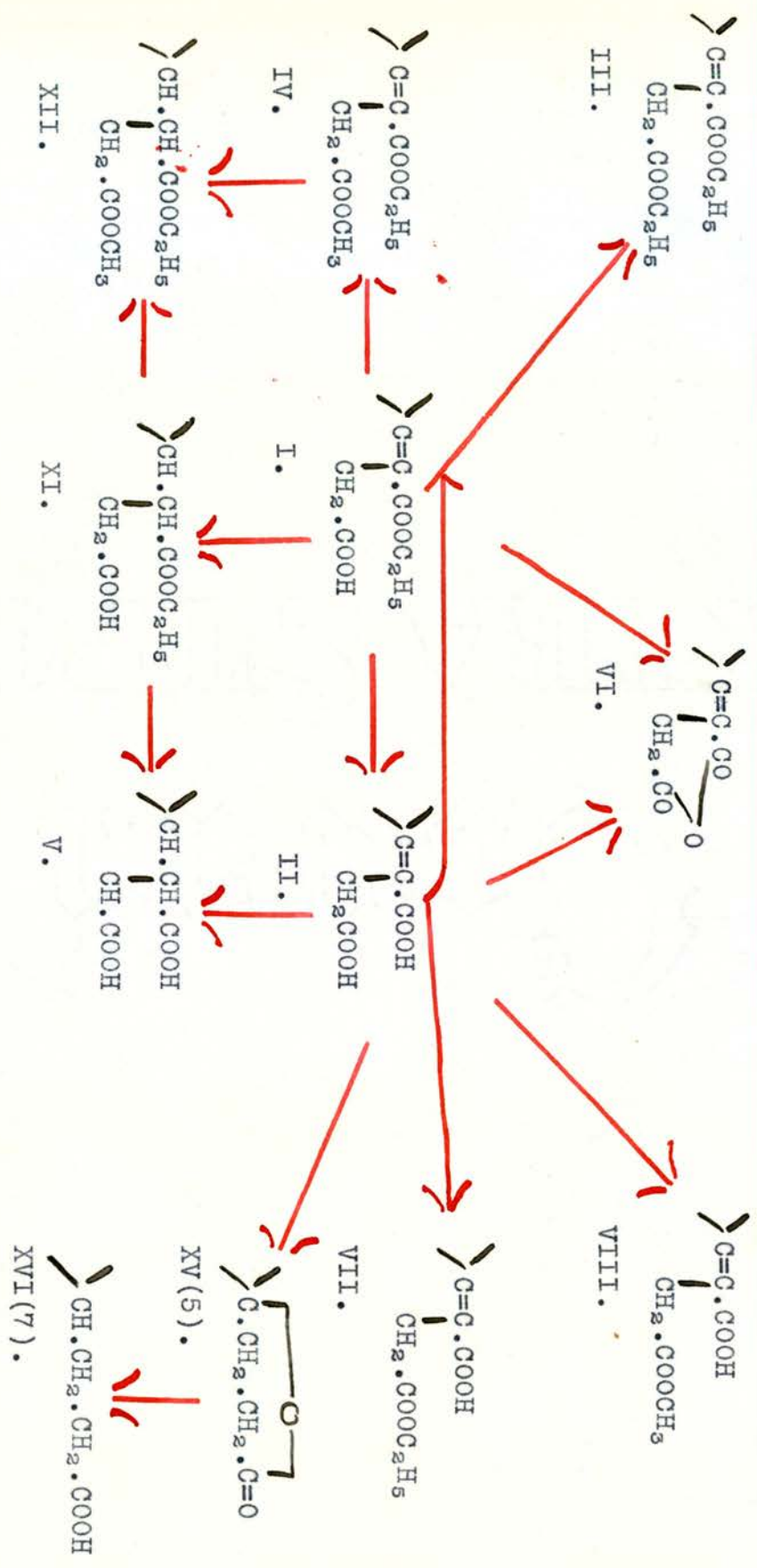
In these diagrams the 9:9'-fluorenyl radical normally represented thus:-

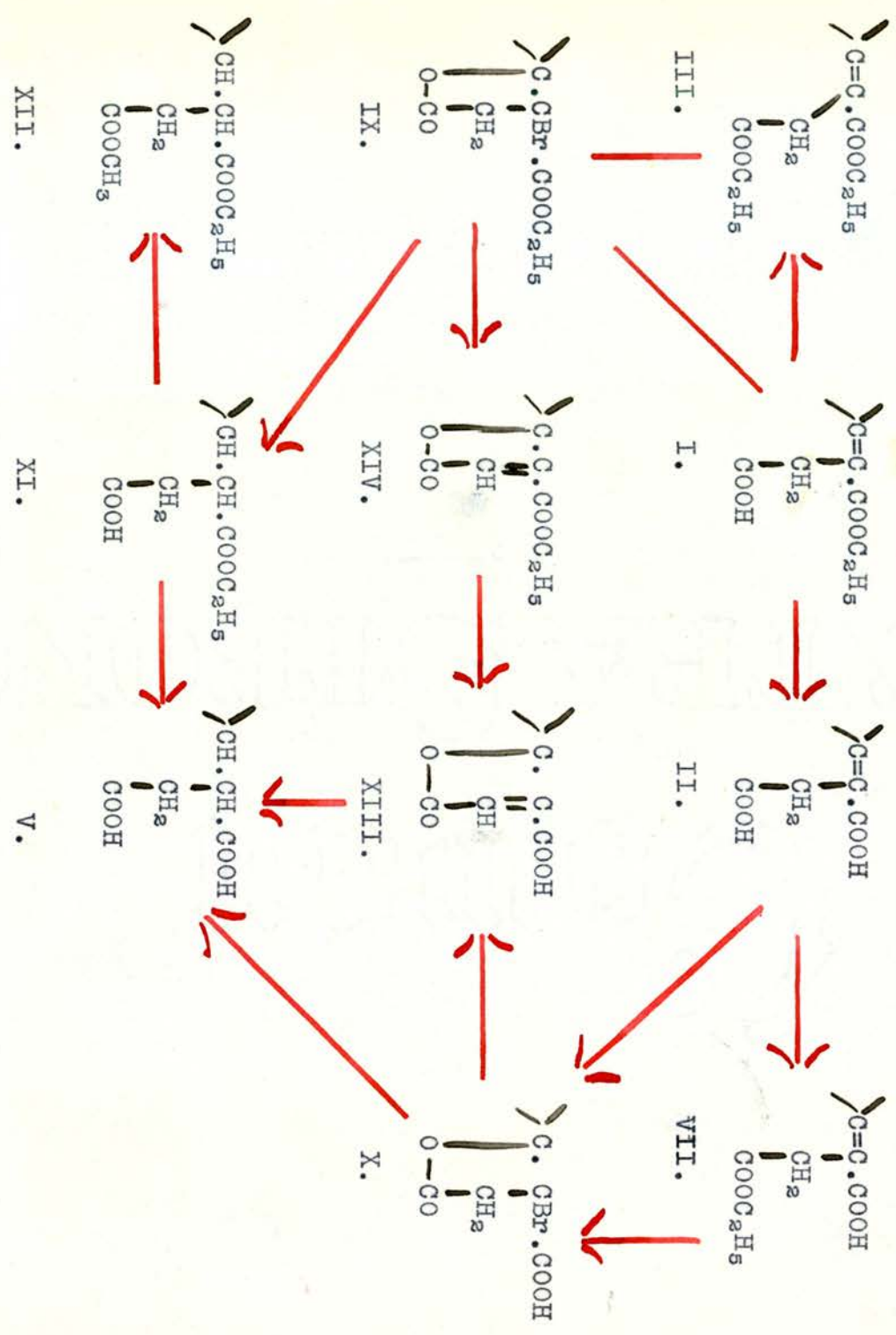


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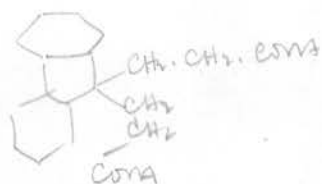


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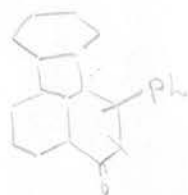
p. 105. 175. 176. 6, 7.

174. 104

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Syn (1) Ring-closure mit HF



(2) Prep. 7



in larger quantities